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11. The specimen shown in Figs. 1 and 2 is a holotype, Academy of Natural Sciences of Philadelphia (ANSP) number 20053, a virtually complete left scapulocoracoid and cleithrum. The articular surface of the glenoid fossa is incomplete posteromedially. The specimen is relatively undistorted and is preserved in three dimensions. A referred specimen, ANSP 20054, is another left cleithrum. It includes a complete dorsal blade but lacks regions ventral to the base of the anteroventral process. The lateral surface of the blade is exposed. This specimen is also undistorted.
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Fullerenes in the 1.85-Billion-Year-Old Sudbury Impact Structure

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Fullerenes (C_{60} and C_{70}) have been identified by laser desorption, laser desorption post-ionization, and high-resolution electron-impact mass spectrometry in shock-produced breccias (Onaping Formation) of the Sudbury impact structure in Ontario, Canada. The C_{60} isotope is present at a level of a few parts per million. The fullerenes were likely synthesized within the impact plume from the carbon contained in the bolide. The oxidation of the fullerenes during the 1.85 billion years of exposure was apparently prevented by the presence of sulfur in the form of sulfide-silicate complexes associated with the fullerenes.

The discovery and synthesis of fullerenes (*1*), and their unusual stability against photodissociation and thermal degradation (*2*), soon led to the hypothesis that fullerenes may be ubiquitous and abundant in the universe, particularly in the outflows of carbon stars (*3*). Fullerene molecules (*4*), or perhaps their hydrogenated counterparts (fulleranes) (*5*), have been suggested as carriers of visible diffuse interstellar bands, although so far spectroscopic searches for fullerenes and fulleranes in space have led to negative results. Fullerenes have been reported in impact residues in a small crater on NASA's Long Duration Exposure Facility (*6*). Several studies have investigated fullerenes in meteorites (*7*), but so far none have been detected (*8*). On the Earth, natural fullerenes have been identified in fulgurite (*9*), a glassy rock that forms where lightning hits the ground, and shungite (*10*), a highly metamorphosed carbon-rich rock within Precambrian sediments. Preliminary results also suggest that trace quantities of fullerenes may be present in sedimentary deposits associated with the Cretaceous-Tertiary impact event (*11*), possibly produced during global conflagnation. Based on these reported terrestrial occurrences, it would appear that fullerenes are not a ubiquitous form of carbon on Earth.

Because fullerenes form under highly energetic conditions and at intense temperatures and pressures, we decided to investigate meteorite impact deposits on Earth for the presence of natural fullerenes. We report here the discovery of fullerenes (C_{60} and C_{70}) in a unit of shock-produced impact breccias (Onaping Formation) from the Sudbury impact structure in Ontario, Canada. The fullerenes were identified in separate samples by laser desorption and laser desorption post-ionization time-of-flight (TOF) methods and by high-resolution electron-impact mass spectrometry (EIMS).

The Sudbury structure (*12*) is an elliptical basin 60 km long and 27 km wide, elongated in an east-northeast direction. Ore deposits occur around the margins of the basin and in radial dykes emplaced into older rock. The outer margin of the basin is outlined by the Sudbury Nickel Irruptive, an igneous body that directly overlies deposits of copper-nickel sulfides. To the north and west, the structure is underlain by older Archean granitic and migmatitic rocks of the Superior Province, while to the south and east the rocks are predominately Proterozoic metasedimentary and metavolcanic rocks of the Huronian Supergroup and felsic plutonic rocks of similar age (*12*). Samarium-neodymium isotopic data on whole rocks and minerals and uranium-lead studies of zircons within the Sudbury complex indicate a formation age of ~1850 million years ago (Ma) (*13*). The proposal that the Sudbury structure was produced by a large meteorite impact is supported by the identification of shatter cones (distinctive conical fractures that are extensively developed in the target rocks), a variety of shock-induced petrographic features in basement rocks and in the overlying Onaping Formation (*14–16*), and by comparison with other structures in which an impact origin is either proven or strongly suggested (*17, 18*).

The Onaping Formation is an 1800-m-thick unit interpreted as allochthonous breccia formed during the impact event and redeposited in the resulting crater (*14–16*), but it differs from the ejecta at other impact craters in being highly carbonaceous (total organic carbon of ~0.5 to 1.0%), especially in the upper parts of the formation. The source of the carbon has long been (and still is) a mystery. In addition to being enriched in carbon, the Onaping Formation contains numerous fragments of devitrified glasses and shocked rocks. There is also evidence for sulfide enrichment from the melting of crustal rocks by the impact event to produce the Sudbury magmas that generated the ores in the lower part of the structure (*19*).

We examined three samples of the carbon-rich upper unit, the so-called "Black Tuff." The samples were collected from

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outcrops about a mile apart in Dowling and Levack Townships, in the northwest corner of Sudbury basin (Table 1). Samples CSF-66-43 and CSF-66-36 are from a road cut at High Falls, on the Onaping River (Dowling Township), which is a type locality for this member. Sample CSF-68-182 is similar to the High Falls materials but contains several large (centimeter-sized) shocked and melted inclusions.

Table 1. Summary of the location and estimated C_{60} content of Sudbury (Onaping Formation) impact deposits. Samples were Soxhlet extracts of powdered rock for CSF-68-182 and of acid residues for CSF-66-36 and CSF-66-43. The C_{60} contents were determined by comparison of the C_{60} peak intensities in the mass spectrum of the sample extracts with those of C_{60} solutions of known concentration.

Sample	Location	C_{60} content (ppm)
CSF-68-182	High Falls	1
CSF-66-36	High Falls	6 to 7*
CSF-66-43	Onaping River	10*

*These values are estimates based on the C_{60} content of the acid residue and the percent acid residue in the bulk sample.

Samples were extracted and prepared for analysis by standard techniques (*20–22*). Separate Onaping extracts were analyzed by laser desorption (*23, 24*) and laser desorption post-ionization (*25, 26*) TOF mass spectrometric techniques. The laser desorption (reflectron) TOF mass spectrum for CSF-66-43 (Fig. 1) shows a strong peak at a mass-to-charge ratio (*m/z*) of 720 atomic mass units (amu), which corresponds to $C_{60}{}^+$, and a less prominent peak at *m/z* 840 amu, which corresponds to $C_{70}{}^+$. Also apparent are peaks (see insert of Fig. 1) at *m/z* of 720, 721, and 722 amu that are characteristic of the isotopic distribution of C_{60}. The spectrum consists almost entirely of $C_{60}{}^+$, and the observed $C_{60}{}^+/C_{70}{}^+$ peak ratio is 15. We were also able to detect a peak at *m/z* of 720 amu and a peak for *m/z* of 840 amu in extracts of CSF-66-36 and CSF-68-182 using the same operating parameters (*23*). In addition, a weak signal for *m/z* of 720 amu was obtained for these extracts by laser desorption directly off of the powdered substrate slurried in a drop of toluene and evaporated to dryness on a slide. A laser desorption (linear) TOF mass spectrum for a separate sample of CSF-66-43 (Fig. 2) shows a strong peak for *m/z* of 720 amu and several lower molecular peaks at *m/z* of 64, 96, 128, 160, 192, 224, 256, 288, and 320 amu that correspond to elemental sulfur [S_2 to S_{10} isotopic measurements confirmed by Fourier transform mass spectrometry (FTMS)] but the peak at *m/z* of 840 amu was not observed (*23*). Moreover, we analyzed a separate sample of the CSF-66-43 extract using laser desorption post-ionization TOF mass spectrometry (*25, 26*). In post-ionization, the molecular-ion yield and degree of fragmentation are sensitive to the wavelength used and the laser intensity. With increasing laser fluence, the fragmentation of $C_{60}{}^+$ was observed with the sequential loss of C_2 fragments dominating the spectrum, a characteristic of the C_{60} molecule (*27*).

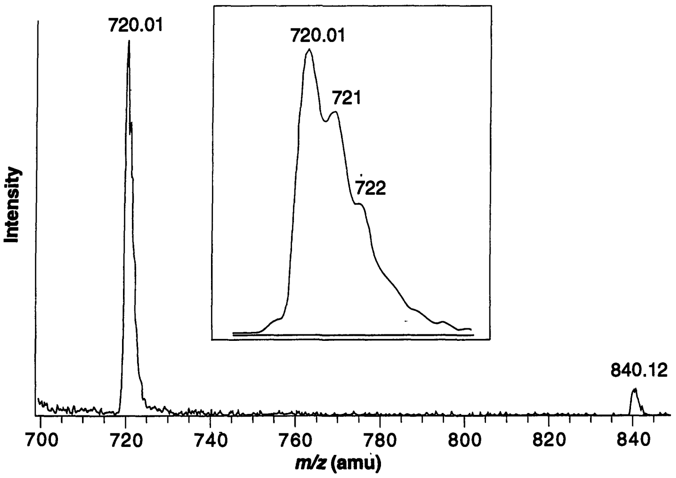

Fig. 1. Laser desorption (reflectron) TOF mass spectrum for CSF-66-43 showing a strong peak at *m/z* of 720 amu and a less prominent peak at *m/z* of 840 amu. An insert of the $C_{60}{}^+$ peak shows the isotopic distributions for *m/z* of 720, 721, and 722 amu (*m*/Δ*m* ~800). Intensity is given in arbitrary units.

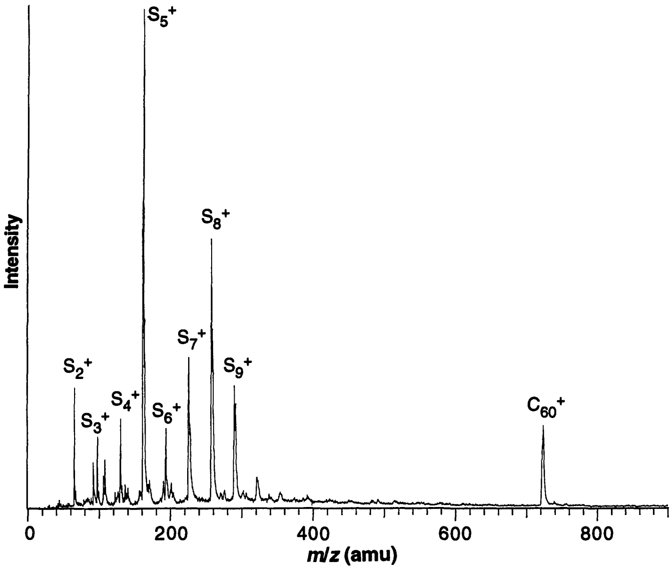

Fig. 2. Laser desorption (linear) TOF mass spectrum for a separate sample of CSF-66-43 showing a strong peak for *m/z* of 720 amu and several lower molecular peaks at *m/z* of 64, 96, 128, 160, 192, 224, 256, 288, and 320 amu that correspond to elemental sulfur (S_2 to S_{10} isotopic measurements confirmed by FTMS). Intensity is given in arbitrary units.

To confirm further the identification of C_{60} in the Onaping Formation, we investigated the CSF-66-43 extract by EIMS using a KRATOS MS50 (*28*). Three peaks were seen at *m/z* of 784, 785, and 786 amu, respectively, but no peaks were evident in the 720-amu region. This finding was surprising considering the laser mass spectrometry results that indicate the presence of fullerenes and elemental sulfur only. We realized that C_{60} could be reacting with the sulfur during the ionization process, resulting in a mass spectrum for $C_{60}S_2$ (*m/z* of 784 amu). Fullerenes dissolve in molten sulfur with maximum fullerene solubilities between 1 and 3 weight % [3 to 11 fullerene molecules per 1000 S_8 molecules (*29*)]. Sulfur and fullerenes dissolve simultaneously in CS_2 and, when treated with copper, transform into near pure fullerene solutions by contact at room temperature (*30*).

We redissolved the sample extract in CS_2 and gently stirred the solution in the presence of copper at room temperature overnight to remove sulfur from the extract. The mass spectrum (Fig. 3) of the treated solution revealed three peaks at 719.9985, 721.0046, and 722.0197 amu corresponding to ${}^{12}C_{60}{}^+$, ${}^{12}C_{59}\,{}^{13}C^+$, and ${}^{12}C_{58}\,{}^{13}C_2{}^+$, respectively. The detection of C_{60} in the CSF-66-43–treated extract by EIMS provides further evidence that C_{60} is present in the samples (*28*). The ratios of the C_{60} isotopic mass peaks are 1:0.71:0.34, suggesting a possible enrichment of ${}^{13}C$. Independent measurements (see insert of Fig. 1) of CSF-66-43 also showed a similar ${}^{13}C$ enrichment. Isotopic compositions measured by stepped combustion have shown that synthetic C_{60} is slightly enriched in ${}^{13}C$ in comparison with the graphite rods from which it was made (*31*). The ^{13}C enrichment we have found in the Sudbury C_{60} may be the result of isotopic fractionation during the synthesis of fullerenes in the impact event or ^{13}C enrichment in the source carbon.

The C_{60} content (see Table 1) of the Onaping Sudbury whole rock samples is in the range of a few parts per million (ppm). The C_{70} content of the rocks is about a factor of 15 less than the C_{60} content. The Onaping Sudbury samples appear to be enriched in C_{60} in comparison to other natural terrestrial occurrences such as fulgurite (9) and shungite (*10*), although no actual concentration values for these latter occurrences have been reported. Because of the extensive area of the Sudbury deposits, this may be one of the largest natural occurrences of fullerenes found so far on Earth (*32*).

The distributions of carbon and sulfur in the Sudbury structure were likely the result of an impact event (*12–19*). The abundance of sedimentary carbon in the Sudbury target rocks is much less than 1%, with an additional 3 to 5% in some rare, thin-bedded, carbonate-bearing sediments, thus eliminating the possibility of a significant carbon source from these surface rocks. Thus, the combustion of these carbonaceous surface rocks, especially at the low atmospheric oxygen partial pressures characteristic on the Earth 1850 Ma (*33*), seems an unlikely mechanism of formation for the Sudbury fullerenes. The carbon that was eventually transformed into fullerenes likely came from a carbon-rich impactor. Fullerenes may have been present in the impacting meteorite, although this seems unlikely because fullerenes have not been detected in carbonaceous chondrites. The presence of fullerenes in carbonaceous chondrites is also thought to be improbable because the formation of fullerenes is inhibited by the presence of hydrogen (*7*), which is abundant in cosmochemical environments. Another possibility is that fullerenes may have formed as a result of the pyrolysis of organic matter [polycyclic aromatic hydrocarbons (PAHs) and kerogen] present in the meteorite. Fullerenes have been synthesized by the pyrolysis of naphthalene at ~1000°C (*1*). A variety of PAHs have been identified in meteorites including naphthalene, phenanthrene, pyrene, fluoranthene, benzfluoranthene, and coronene (*7, 34*). All of these PAHs have been suggested as possible precursors to the formation of fullerenes in the gas phase (*1, 35*).

It has been suggested that organic carbon may have formed on the early Earth by the recombination of reducing mixtures resulting from the shock vaporization of carbon-rich bolides upon impact or by impact shocks with the surrounding "target" rocks (36). Carbon onions and perhaps fullerenes may have formed in a similar manner (8). The organic carbon within the vapor plume resulting from impact would have been nearly entirely converted to CO (36). Recent efforts to synthesize molecular forms of carbon from carbon oxides showed that carbon oxides undergo a loss of CO molecules to form cyclocarbon ions and large carbon cluster ions (*37*). Although it is intriguing to suggest that the organic carbon (PAHs, kerogen, carbon oxides) present in the bolide may have been converted to carbon clusters and perhaps fullerenes upon impact, subsequent metamorphism sustained by the Onaping Formation after deposition (greenschist facies probably involving temperatures of 300° to 400°C at pressures of 3 to 5 kilobars) may also have transformed organic compounds with time (*12, 14–16*).

Fullerenes degrade quickly at fairly low temperatures when exposed to air (*38*). The survival of fullerenes found in the 1850-Ma Sudbury deposits clearly requires storage in an environment of low oxygen. Although low oxygen levels were present in the Earth's atmosphere at the time of the Sudbury fullerene synthesis, oxygen probably reached present atmospheric levels soon (a few hundred million years) after deposition (*33*). The presence of diagenetic sulfides indicates that the environment in which the Onaping rocks were deposited had low oxygen and high sulfur concentrations.

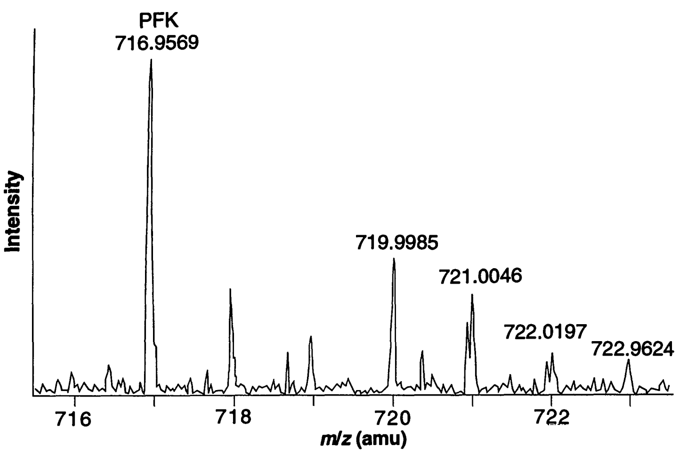

Fig. 3. Electron ionization mass spectrum ($m/\Delta m$ ~10,000) of $C_{60}{}^{+}$, revealed three peaks at *m/z* of 719.9985, 721.0046, and 722.0197 amu corresponding to $^{12}C_{60}{}^{+}$, $^{12}C_{59}{}^{13}C^{+}$, and $^{12}C_{58}{}^{13}C_{2}{}^{+}$, respectively. Intensity is given in arbitrary units.

Field-emission scanning electron microscopy analyses of a sample of Onaping tuff indicate an enrichment of carbon (up to 3 weight %) in association with sulfide-silicate complexes, with lesser amounts (<1%) in the fine-grained matrix. Perhaps the fullerenes in the Onaping rocks were protected from oxidation by the surrounding sulfide-silicate matrix in which they are contained, allowing fullerenes to survive to present. This possibility may also explain the presence of fullerenes within "yellowish-brown" fracture filling films in shungite (*10*).

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28. Mass spectra were collected under electron-impact conditions at 70 eV, an accelerating voltage of 8 kV, a source temperature of 200°C, and a direct in-source heated probe ramped to 700°C at 100°C per minute. An important fact regarding EIMS is that C_{60} is not produced in the mass spectrometry process; therefore, the C_{60}^+ ion detected is present in the original sample.
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Fullerenes in the Cretaceous-Tertiary Boundary Layer

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High-pressure liquid chromatography with ultraviolet-visible spectral analysis of toluene extracts of samples from two Cretaceous-Tertiary (K-T) boundary sites in New Zealand has revealed the presence of C_{60} at concentrations of 0.1 to 0.2 parts per million of the associated soot. This technique verified also that fullerenes are produced in similar amounts in the soots of common flames under ambient atmospheric conditions. Therefore, the C_{60} in the K-T boundary layer may have originated in the extensive wildfires that were associated with the cataclysmic impact event that terminated the Mezozoic era about 65 million years ago.

When fullerenes were discovered to be formed spontaneously in condensing carbon vapors (*1*), it was suggested that they might be widely distributed in the universe. Subsequent searches for fullerenes in interstellar media and meteorites (*2, 3*) have thus far been unsuccessful, but C_{60} and C_{70} have been reported to occur in samples of shungite, a meta-anthracite coal from a deposit near Shunga, Russia (*4*), and in fulgurite, a substance formed when lightning strikes certain soils or rocks (*5*). The occurrence of fullerenes in shungite is surprising because the only routes to fullerenes discovered thus far in the laboratory have involved gas-phase chemistry at temperatures of more than 1000°C. Shungite is thought to have formed from carbonaceous material creeping into fissures of a Precambrian rock that metamorphosed under extreme pressures; hence, either the original material already contained fullerenes, or these must have formed during the metamorphism by as yet unknown solid- or liquid-phase mechanisms.

Here we describe a search for ancient

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