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23. Laser desorption mass spectra (LDMS) were obtained with a KRATOS (reflectron) TOF instrument and a separate (linear) TOF instrument constructed at Argonne National Laboratories (*24*), both with mass resolution ($m/\Delta m$) of up to 2000. Mass (m) spectra of positive ions emitted directly in the desorption process from the sample were collected at a low power level. Blanks were run between each sample analysis. Standards of C_{60} and C_{70} (Aldrich) were used to calibrate measurements of fullerenes detected in the sample extracts. A microliter of concentrated solution was placed on a stainless steel slide that was transferred by a rapid sample change port into the high vacuum chamber (~2×10^{-7} to 2×10^{-8}). Neutral and ionized particles were desorbed by a 337-nm ultraviolet nitrogen laser at low power densities (10^6 W/cm^2) similar to power densities used to analyze fullerenes in shungite (*10*) and fulgurite (*9*). The C_{60}^+ isotope was readily detected in all of the sample extracts; however, C_{70}^+ was not. This difference may mean that C_{70}^+ is not as stable as C_{60}^+ and is, therefore, present at much lower concentrations, making it more difficult to detect. We also observed extreme heterogeneity in the sample extracts once they were allowed to dry on the slide such that fullerenes were not present at every position analyzed. This heterogeneity was also observed with standard C_{60} solutions and is apparently a solvent evaporation artifact. Fragments at C_{58}^+ and C_{56}^+ and several low-mass carbon clusters (C_5^+ to C_{28}^+) were observed at power levels much higher than what was originally used to detect C_{60}^+ in the Onaping extracts. Despite the increased power levels needed to fragment C_{60}^+, no higher carbon clusters were observed, indicating that C_{60}^+ was not formed in the desorption process.
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27. A potential problem for laser desorption and laser desorption post-ionization TOF techniques is that under certain conditions fullerenes can be generated by the laser process (*24–26*). Because there is essentially no carbon in any of the Sudbury target rocks (*12–16*), we examined several other geological (carbonaceous) samples including coal, hydrothermal sediments (hydrocarbons), Green River Oil Shale, soot from burned wood (Malibu fires), and burned oil (Norwegian crude). Mass spectra of these samples were free of C_{60}^+ and other fullerene peaks, verifying that, under our experimental conditions (*23–25*), fullerenes were not generated during the desorption or desorption post-ionization processes.
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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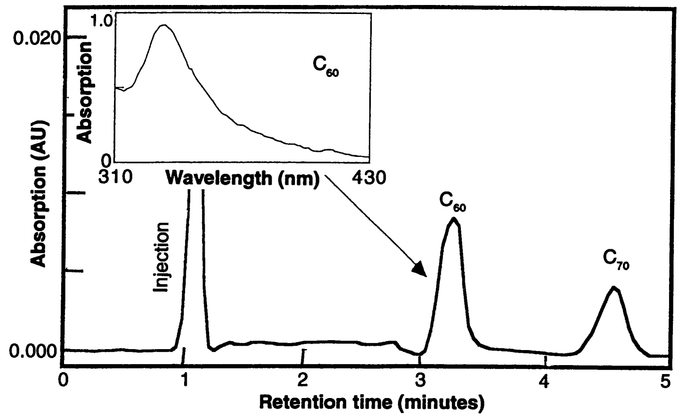

Fig. 1. Chromatogram, deduced from UV adsorption at 330 nm, of the simultaneous injection of 49.5 ng of C_{60} and 57.75 ng of C_{70} (both synthetic). The mobile phase was methanol:toluene 50:50. The peak at 1.17 min is due to the injection of pure toluene. The peaks at 3.20 and 4.44 min are due to C_{60} and C_{70}, respectively. The insert shows the absorption spectrum of C_{60} taken at 3.20 min. AU, arbitrary units.

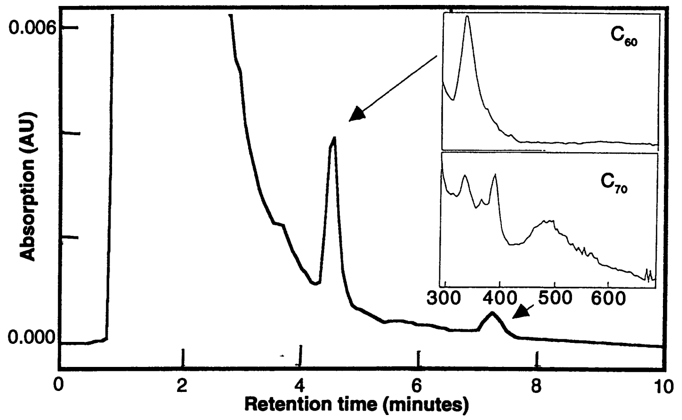

Fig. 2. Chromatogram of the toluene extract of the soot from a toluene burn. Note that the fullerene peaks appear for this condition at about 4.5 and 7.1 min, because the mobile phase was methanol:toluene 55:45 to elute the fullerenes further away in time from the massive PAH peak (height 1.30 μV). The absorption spectra of the fullerenes are shown for the range 290 to 650 nm. AU, arbitrary units.

fullerenes produced by natural processes on Earth, and we also report the results of an experiment that prompted us to speculate that a possible source might involve the burning of carbonaceous matter. A particularly good candidate for such a search would be the soot- and iridium-rich seams at the K-T boundary, because the abundant soot in these well-characterized deposits is thought to have been derived from worldwide wildfires after a large meteor impact 65 million years ago (6).

Previous analyses of soots for the presence of fullerenes have generally used mass spectrometry of either laser-vaporized or thermally heated samples (*7–9*). One problem with these methods is that at concentrations of a few parts per million (ppm), fullerenes may not volatilize efficiently from the surrounding soot, and the high temperature and gas-phase conditions required in the sampling may inadvertently produce fullerenes that were not originally present in the sample. Instead we used high-pressure liquid chromatography (HPLC) of toluene extracts together with direct photodiode array detection of the ultraviolet (UV)-visible absorption spectrum of the separated fullerenes. With commercial HPLC units (*10*) this technique is capable of detecting as little as 0.2 ng in an injected sample while avoiding high temperature, gas-phase conditions. Figure 1 shows such a HPLC chromatogram detected at 330 nm of a standard solution of ~50 ng of C_{60} and C_{70} injected in toluene; it has excellent resolution and signal-to-noise ratio. The insert shows the characteristic absorption spectrum recorded at the retention time of C_{60}.

As predicted by Zhang *et al.* (*11*), fullerenes are produced in at least small amounts in some sooting flames (*12, 13*), but analyses of a variety of commonly occurring soots have failed to detect the presence of fullerenes (*7, 8*). Thus far only one study has reported the recovery of fullerenes from a free-burning flame (9). To verify this report, we used the HPLC analytical technique for the detection of fullerenes in soots from free-burning toluene and candle flames in air at normal atmospheric conditions. A small pool of toluene in a glass dish was ignited and the resultant soot was collected. We extracted this soot by sonication in fresh toluene at room temperature and filtered and concentrated the resultant solution. HPLC analyses (Fig. 2) showed that the dissolved matter was composed primarily of polycyclic aromatic hydrocarbons, but that C_{60} and C_{70} were also present. The amount of $C_{60} + C_{70}$ typically extracted from soot from the burning of toluene in air ranged from 25 to 50 ppm. Even the soot from a common decorative candle contained fullerenes at the concentration of 1 to 10 ppm, as determined by an analogous method.

These results suggest that fullerenes may be produced at detectable levels in naturally occurring fires and may still be found in ancient deposits. Perhaps the most extensive combustion to have occurred in Earth's history was the result (putatively) of a meteor impact near Chicxulub in the Yucatán Peninsula of Mexico about 65 million years ago, as evidenced by iridium- and soot-rich seams at the K-T boundary worldwide (6). We have analyzed carbon-rich samples of this boundary layer from two sites in New Zealand. At the first, Woodside Creek, the K-T boundary appears as a heavily weathered shale located between massive Cretaceous and more thinly bedded Tertiary limestones (*14*). The Tertiary limestone beds are parted by thin layers of shale. At the second site, Flaxbourne River, about 10 km from Woodside Creek (*14*), the boundary layer is marked by a much less weathered clay richer in $CaCO_3$ than the shale at Woodside Creek. At Flaxbourne River, the boundary clay has a gray or a nearly black appearance. Both gray and black seams were sampled. At Woodside Creek and at Flaxbourne River the iridium abundances are 91 and 32 ng/cm^2, the carbon contents after dichromate etch are 4.8 and 3.5 mg/cm^2, and the soot contents of these carbons are 69 and 68%, respectively (6).

We studied two sample sets. The first consisted of gram-sized, still pristine samples collected 10 years ago. When toluene extracts from these samples showed evidence for the presence of C_{60}, we collected a fresh and much larger set of samples at the Woodside Creek and Flaxbourne River outcrops. At that time we also collected control samples from the Cretaceous limestone immediately below and of Tertiary shale partings 57 cm above the K-T boundary.

All samples were digested with toluene at room temperature in an ultrasonic bath for at least 8 hours, filtered, and then concentrated to 1.0 ml or less. We took precautions throughout the procedure to prevent contamination of the rock samples and extracts with modern fullerenes. Sample storage, crushing, grinding, extraction, evaporation, and filtration were done in a laboratory that had never been used to analyze fullerenes. All procedures, glassware, chemicals, and the HPLC system were checked with procedural and instrumental blanks.

The HPLC analysis was performed under similar conditions to those discussed for the toluene soot. We tested 37 procedural blanks, none of which yielded fullerenes above the minimum detectable limit of 0.2 ng. All sample results are listed in Table 1. All boundary samples have significant peaks at the expected retention time of C_{60}, but the Cretaceous limestone and Tertiary shale were free of C_{60} and C_{70}. This result shows that contamination of the boundary samples is not

Table 1. Results of HPLC analysis. The fourth column lists C_{60} amounts in the clay. The numbers in the fifth column were deduced from published surface densities of the boundary layers (*6*). For the Flaxbourne River samples, gr, gray seam; bl, black seam.

Sample	Weight of sample (g)	Weight of C_{60} in sample (ng)	Concentration of C_{60}	
			ng/g	ng/cm^2
		Woodside Creek		
Cretaceous limestone*	127.7	0	0	0
Tertiary shale*	135.6	0	0	0
K-T Clay	3.497	7.6	2.17	2.4
K-T Clay	3.323	9.1	2.74	3.6
K-T Clay*	123.9	309	2.5	3.3
K-T Clay*	201	994	4.7	6.2
K-T Clay*	112.3	609	5.4	7.1
K-T Clay*	68	22.1	0.325	1.4
		Flaxbourne River		
K-T Clay (gr)	1.980	1.1	0.556	2.5
K-T Clay (gr)*	57.2	65.5	1.14	5.0
K-T Clay (gr)*	200	11.6	0.058	0.26
K-T Clay (bl)*	68	160	2.3	10.3
K-T Clay (bl)*	200	369	1.84	8.1

*Samples collected in December 1993.

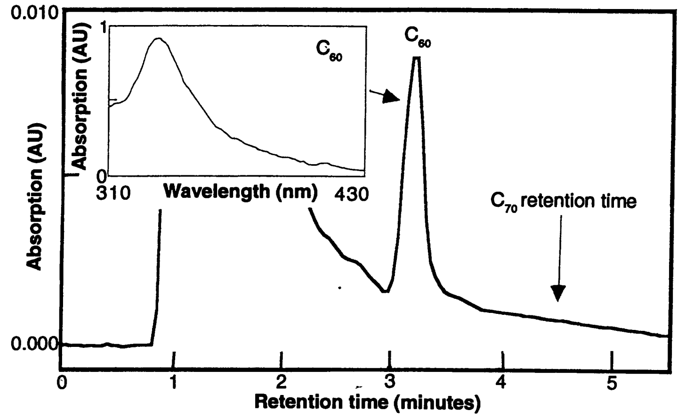

Fig. 3. Chromatogram of a concentrated toluene extract from the 112.3-g sample of the Woodside Creek K-T boundary rock. The large peak after 1 min is due to the injection of solvent but also to comparatively polar hydrocarbons. The peak at 3.18 min is consistent with the retention time of C_{60}, and the absorption spectrum taken at this time (insert) is identical to that of Fig. 1. Absorption spectra taken nine times in the range 1.26 to 3.50 min (*18*) show that this distinct spectrum occurs only in the range 3.00 to 3.30 min. No significant signal is present at the retention time of C_{70}; the upper limit of the C_{70}/C_{60} ratio of the injected sample is 0.002. The very small shoulder at 2.8 min may be due to $C_{60}O$, which may have occurred in the rock before collection but may also have formed from C_{60} afterwards by reaction with ozone of the current ambient atmosphere.

likely to have occurred. There was no systematic difference of C_{60} contents between the decade-old and recent samples. Apparently, 10 years of exposure to air and light has not substantially reduced the C_{60} contents of the samples.

The extracts from these gram-sized samples did not contain enough C_{60} to yield convincing absorption spectra for this fullerene, but those from the larger, fresh samples did. The chromatogram of such an extract from K-T clay at Woodside Creek is shown in Fig. 3. Both the C_{60} peak retention time and absorption spectrum are identical to those of the synthetic fullerene sample in Fig. 1. The analyses of all extracts from samples heavier than 100 g showed this same spectrum. At the expected retention time of C_{70} no significant signal was found; the upper limit of the C_{70}/C_{60} ratio was 0.002. Extracts from the clay at Flaxbourne River showed a small peak at this retention time, but the amounts of C_{70} were too small to yield an acceptable absorption spectrum (*15*). The net fullerene contents of the rocks range from 0.3 to 5.4 ppb by weight (Table 1). The gram-sized samples from the two sites were demineralized before extraction; hence, their C_{60} content per gram of carbon-bearing matter (which is about 70% soot) could be estimated. The result for these samples was about 0.1 to 0.2 ppm of C_{60}, which is reasonable on the basis of our measures of the typical amount of fullerenes in soots from open flames.

Our results indicate that fullerenes have long been part of our natural environment and that they can survive, at least in some protected deposits, for geologic time scales (*16*). It is, of course, conceivable that the K-T C_{60} came to Earth with the impactor of the Chicxulub crater, but how would these fullerenes have survived exposure to very hot SO_2 generated in vast amounts by the impact (*17*)? We suggest that the K-T fullerenes were formed locally by post-impact sooting wildfires at a later time when the concentrations of reactive gases in a cooler atmosphere were much decreased.

Although we found C_{70} in flames produced in the laboratory and in the clay from Flaxbourne River (*15*), it is virtually absent from the clay at Woodside Creek. Either some natural process produces C_{60} almost to the exclusion of C_{70}, or else a process exists by which C_{70}, but not C_{60}, was quantitatively destroyed in the 65 million years since the deposition of the boundary layer at Woodside Creek. The presence of C_{70} in the K-T boundary clay at Flaxbourne River is more consistent with the second proposal (*18*).

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