Fullerenes from the Geological Environment

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By means of high-resolution transmission electron microscopy, both C_{60} and C_{70} fullerenes have been found in a carbon-rich Precambrian rock from Russia. The fullerenes were confirmed by Fourier transform mass spectrometry with both laser desorption and thermal desorption/electron-capture methods to verify that the fullerenes were indeed present in the geological sample and were not generated by the laser ionization event. The mass spectra were measured under conditions sufficient to resolve the $^{13}C/^{12}C$ isotopic ratios for C_{60} and C_{70} and indicate that these ratios correspond to the normal range of isotopic values.

Fullerenes were discovered as an outgrowth of an investigation of carbon clusters that presumably occur in interstellar atmosphere (*1, 2*). Subsequent studies were made with the goal of locating them in meteorites (*3–6*), but the searches have been unsuccessful. In spite of the intensive research that has occurred since it became possible to make fullerenes in macroscopic quantities (*7, 8*), there are no confirmed occurrences of fullerenes formed in the natural environment. In the laboratory they have been synthesized by laser ablation (*9*), in carbon arcs (*7*), and by burning benzene (*10*). Their apparent absence is perhaps not surprising because they are synthesized at temperatures greater than occur in the natural environment outside of extreme conditions (lightning strikes, stellar interiors). Another constraining factor in natural environments is the effect that oxygen, nitrogen, and other non-inert gases have on inhibiting the growth of fullerenes.

Here we report an occurrence of fullerenes from the geological environment. We found them while examining high-resolution transmission electron microscopy (HRTEM) images of poorly graphitized material by noticing the similarity to images of synthetic fullerenes (*11*). We subsequently confirmed the presence of C_{60} and C_{70} by mass spectrometry. They occur within fracture-filling films in shungite, an usual carbonaceous rock found near the town of Shunga in Karelia, Russia.

Shungite has been the subject of intensive investigation for over a century (*12, 13*). It occurs in a metamorphosed carbon-rich rock within Precambrian sediments; the host formations are, according to Volkova and Bogdanova (*14*), seams of sedimentary origin. The overlying rocks consist of gray dolomitized sandstones and poorly sorted silts and clays, and the underlying rocks are not exposed. The shungite consists of masses containing up to 99% carbon. Diabase is interstratified with shungite-bearing rocks, and the shungite concentration increases with proximity to the diabase. Our sample comes from inclusions in the diabase.

Based on its optical characteristics, Firsova and Yakimenko (*15*) classified shungite into four groups. Our sample belongs to their shungite 1c group. Volkova and Bogdanova grouped it into five types, based largely on carbon content, mineral matter, and luster. Khavari-Khoransani and Murchison (*16*) simply divided it into "bright" and "dull" varieties based on its appearance in hand specimen; the former has a high luster and higher carbon content whereas the "dull" variety has a matte appearance. Our sample is of the bright variety.

The origin of shungite has been a continuing source of controversy ranging from organic (*14*) to volcanic (*17*). Firsova and Yakimenko (*15*) concluded that shungite formation was strongly affected by metamorphic processes. Volkova and Bogdanova (*14*) believe that it represents ancient coal beds within sediments, and that shungite is the most highly metamorphosed coal known; they point out that it has features typical of both humic and sapropelic coals and shows structures that they interpret as woody remains.

Compositionally, shungite represents coals of the meta-anthracite rank, characterized by low ash and sulfur contents, low volatile yields, and high carbon contents. Although Volkova and Bogdanova (*14*) describe organic features that they interpret as evidence of Precambrian life, the last sentence of their paper curiously raises the possibility that the shungite is not Precambrian in age. Schopf (*18*) believes shungite is "coaly" rather than a proper coal and that it is remobilized material formed by devolatilization of organic remains. If a coal, it would probably be best grouped with the anthraxolites, but it seems more likely that it has its origin from bitumens. Clearly, uncertainty exists regarding this unusual rock type.

There are several examples of Precambrian coals, of all which are of interest because of the potential information they provide about early forms of life (*19–22*). Tyler *et al.* (*19*) report the occurrence of thin, highly reflecting graphitic films in their Precambrian coal samples. It is intriguing to speculate that these veins may also contain fullerenes. We obtained a piece of the material collected by Tyler, but we have not observed any of the veinlets.

The samples we studied are pure black, have high reflectivity (resembling jet or obsidian), conchoidal fracture, and contain small, curling fractures that resemble narrow dessication cracks. The fractures are filled with carbonate. In some cases the fracture walls are coated with thin, dark, yellowish-brown films of carbon that have a submetallic luster. TEM study shows the films

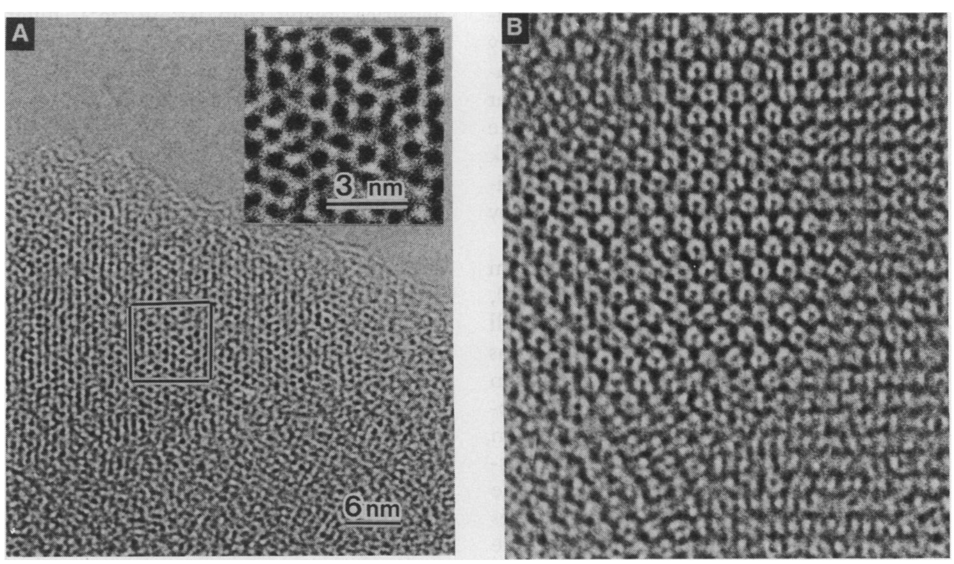

Fig. 1. (**A**) HRTEM image of fullerenes in a shungite sample. The rounded shapes are C_{60} and perhaps C_{70} molecules, arranged in a close-packed array. The inset shows a relatively well-packed array of molecules. (**B**) HRTEM image of synthetic fullerenes at the same magnification as the inset of (A) [S. Wang, Arizona State University]. The contrast between (A) and (B) differs slightly because of small differences in TEM operating conditions.

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