MATERIALS SCIENCE

A First Sighting of Buckyballs in the Wild

Ever since buckminsterfullerene began seizing the imagination of molecular scientists in the mid-1980s, the soccerball-shaped, 60-carbon molecule has been a creature of the lab. But, convinced that nature must have anticipated human artistry, researchers have been hunting for buckyballs in the wild. With this issue of *Science*, the hunt has taken a surprising twist, in a most unlikely place: Shunga, a Russian town in the lake region of Karelia, about 200 miles northeast of St. Petersburg. The region had long been known to geologists for its outcroppings of carbon-rich strata, laid down more than half a billion years ago in the Precambrian era. Now a sample of black, lustrous rock from these ancient beds may make Shunga famous as the first place where buckminsterfullerene has been found in nature.

On page 215, Peter Buseck and Semeon Tsipurksy of Arizona State University and Robert Hettich of Oak Ridge National Laboratory in Tennessee report finding trace amounts of C_{60} and C_{70}—a larger, rugby-ball-shaped molecular cousin—in a single sample of shungite, as the coal-like rock is called. Electron micrographs suggest, and mass spectrometry confirms, the presence of buckyballs in films lining fractures of the rock. But the trio of researchers don't know how they got there, and other fullerene researchers are equally baffled.

A solid rock like shungite is about the last place you'd expect to meet wild C_{60}, says Harold Kroto of the University of Sussex in England, a co-discoverer of C_{60}. To date C_{60} and other fullerenes have only been synthesized in rarefied venues like benzene flames or, as in their original discovery, in the hot plasma formed by blasting a piece of graphite with a laser. Indeed, theory confirms that fullerenes should form only when they have lots of elbow room, says Donald Huffman, a chemist at the University of Arizona, who with co-workers reported the first practical synthesis of fullerenes in 1990. Only where molecules are few and far between will the small chicken-wirelike sheets of carbon atoms generated by some reactions of carbon-rich materials tend to curl around onto themselves, forming individual fullerene cages, instead of bumping into other carbon fragments. In the crowded environment of a solid, by contrast, there's little room for this kind of individualism, says C_{60} co-discoverer Richard Smalley of Rice University; long before the edges of a carbon sheet could cinch together, the sheet would coalesce with other molecular structures into a larger, less ordered network.

Which is why researchers who long for a wild fullerene have focused their hunt on such environments as sooty flames and the carbon-rich molecular clouds around red giant stars. They've also looked in meteorites, which contain samples of interstellar material. In all these seemingly plausible places, they've had no luck. And then along come Buseck, Tsipursky, and Hettich, who seem to have stumbled across the implausible.

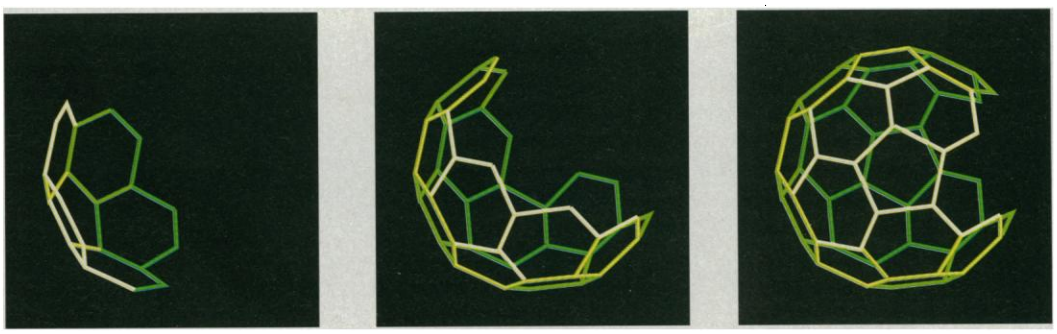
The first hint that C_{60} might live in rocks came last summer when Tsipursky, a mineralogist formerly at the Russian Academy of Sciences in Moscow, was examining high resolution transmission electron microscopy (HRTEM) images of a piece of shungite a Russian colleague had sent him. Most of the images showed either amorphous, ill-ordered arrangements of atoms or patterns reminiscent of graphitic material. "But I found a few honeycomb images that didn't look like graphite," Tsipursky recalls. "They reminded me of fullerenes."

Tsipursky probably never would have made that connection if he had not happened to be sharing an office with microscopist Su Wang. Last year, a few months before Tsipursky was studying his shungite samples, Wang and Buseck were making HRTEM images of films of purified, lab-made C_{60} (*Science*, 28 June 1991, p. 1785). Tsipursky had seen the images, and they looked compellingly like the honeycomb patterns from the shungite.

If the similarity was no mere coincidence and if he wasn't falling victim to mislabeled images or contamination or wishful thinking, Tsipursky knew he was in possession of the first fullerenes ever found in the wild. But there were good reasons for caution. Recalls Buseck: "When he [Tsipursky] brought it [a shungite image] to me last September, I was skeptical," because an HRTEM image by itself can't prove anything about a sample's composition. "We needed a mass spectrum," Buseck said. Mass spectrometry, a sensitive means of "weighing" molecules and their fragments, often enables chemists to infer molecules' atomic compositions.

Routine mass spectrometry at Arizona State University showed a peak at 720 atomic mass units (amu)—the figure you would expect from a buckyball's 60 carbon atoms, weighing 12 amu each. Still, Buseck and Tsipursky wanted more assurance that they weren't fooling themselves before going public with their shungite bombshell. So Buseck enlisted Hettich, a mass spectrometrist at Oak Ridge who has logged a lot of time analyzing synthetic fullerenes, in a blind test.

Last October, Buseck FedExed to Hettich about a dozen unidentified carbon samples, among them synthetic fullerenes, shungite samples, and fullerene-free blanks. When the results came back, the mass spectra of three of the five samples that contained shungite were indicative of fullerenes. To make sure that C_{60} wasn't forming during the procedure—perhaps when the sample was vaporized with a laser—Hettich dimmed the laser to levels at which no one had ever observed fullerenes forming. But the 720-amu peak still dominated the spectra's otherwise bleak baselines—as it did when Hettich turned off the laser and instead used heat to vaporize the samples.



A buckyball is born. Could it happen in solid rock?

SOURCE: SMALLEY CREDIT: SUSAN NOWOSLAWSKI

Barring some unforeseen error, "these experiments definitively establish the presence of fullerenes in our samples," Buseck, Tsipursky, and Hettich conclude. Indeed, odd as the finding seems, the giants of the field are impressed with the evidence. "It does look like C_{60} is in this material," concedes Kroto, adding: "It is the first time we can say it is in nature." His former partner Smalley agrees, suggesting with a smile in his voice that, as a next step, the trio "might find a mine for buckyballs." Far more certain, says Huffman, is the start of a quest to understand how on Earth wild fullerenes ended up in the crevice of a lustrous Russian rock.

–Ivan Amato