The Formation of Fullerenes

The report by Peter R. Buseck *et al.* (10 July, p. 215) of their detection of fullerenes in samples of Karelian shungite is remarkable and intriguing. In the Research News summary (p. 167) of that work, Ivan Amato cites comments by Harold Kroto, Donald Huffman, and Richard Smalley concerning the environment in which these fullerenes might be expected to form. The underlying arguments used or implied by Amato's sources are essentially kinetic, dealing, for instance, with the rate at which a sheet of carbon atoms might curl to form a fullerene molecule, in contrast with rates at which it might form other bonding arrangements. It appears to me, however, that equilibrium thermodynamics could also have provided controlling factors for the formation of these fullerenes.

Buseck *et al.* state that the parent shungite occurs as part of a metamorphic sequence and that "the shungite concentration increases with" [the intensity of thermal metamorphism imposed by the diabase intrusive rock with which the fullerene-bearing samples are associated] (*1*). [I have rephrased their description to bring out its implications for readers with little knowledge of geology.] These features, plus the stated original locations of the shungite samples in which fullerenes were found, suggest that the fullerenes are products of high-grade thermal metamorphism and are present because they have a smaller free energy, under the relevant conditions, than do alternative forms of carbon. Given that millions of years may have elapsed, in Precambrian times, during the cooling of the diabase and its inclusions and contact-metamorphosed wallrocks, kinetic controls such as those referred to in Amato's article could have been less important in determining why these fullerenes formed than they are in laboratory-based experiments. It seems that nature has done an important experiment for us, but we risk misinterpreting its results if we do not keep in mind that time scales of natural (especially geological) processes and those of laboratory experiments are usually very different.

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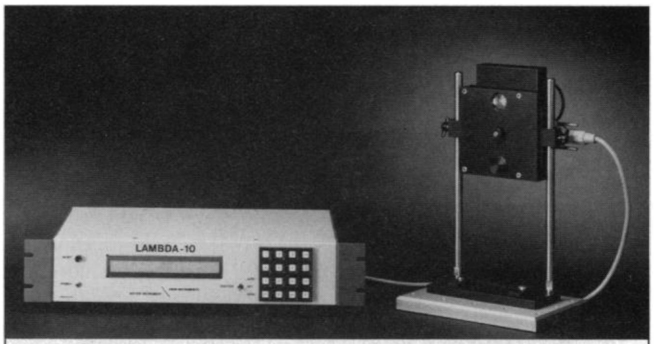
Response: In our paper we imply, on the basis of published literature, that shungite formation is related to thermal metamorphism. However, we know neither whether the fullerenes within the shungite followed an equilibrium path to their formation nor what their precursor material was and whether it had a special structure that favored fullerene formation. Goles makes a plausible point regarding the rate at which reactions can occur in the geological realm. He also makes the reasonable assumption that fullerenes formed slowly as products of metamorphism (in contrast to the rapid formation in all laboratory syntheses reported to date). Fullerenes may be the stable form of carbon under the operative conditions, but may require extended times, high temperatures, or both, to form. The paucity of thermodynamic data precludes a determination of whether fullerenes, like diamonds, are metastable relative to graphite or whether they are kinetically inhibited from transforming because of the energy required to break and reform bonds. Indeed, Ugarte (*1*) suggests that curled carbon rather than graphite may be favored at high temperatures.

Unfortunately, the data from our shungite report are insufficient to resolve the question of stability. However, the scarcity of geological fullerenes that we have encountered in our searches to date is not



suggestive of fullerenes being stable relative to graphite. Also, much of the shungite consists of nominally amorphous carbon, which suggests that even on geological time scales, well-ordered material—be it graphite or fullerenes—does not necessarily form. Clearly, further work is required to understand the conditions needed to produce fullerenes in the geological environment.

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1. D. Ugarte, *Nature* **359**, 707 (1992).

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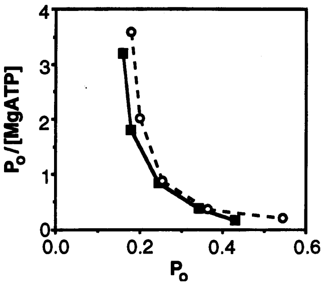
Correction

In the final preparation of the manuscript of our report "Regulation by ATP and ADP of CFTR chloride channels that contain mutant nucleotide-binding domains" (18 Sept., p. 1701) (*1*), we inadvertently plotted the data for figure 1C with an incorrect *x* axis: MgATP was plotted on the *x* axis instead of P_o. We did not immediately notice the error, which was brought to our attention by Charles Venglarik and Robert Bridges, because the shape of the two curves is similiar. The correct plot is shown in the figure below.



In both plots the data do not fit a straight line, which supports our interpretation that more than one site may be involved with adenosine triphosphate (ATP) regulation of the cystic fibrosis transmembrane conductance regulator (CFTR). We regret any inconvenience this may have caused.

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1. M. P. Anderson and M. J. Welsh, *Science* **257**, 1701 (1992).

Corrections and Clarifications

The table accompanying Larry Thompson's Research News article "At age 2, gene therapy enters a growth phase" (30 Oct., p. 744) incorrectly identified the principal investigators of gene therapy trials to treat kidney cancer and malignant melanoma being conducted at Memorial Sloan-Kettering Cancer Center and of a brain cancer experiment at the National Institutes of Health. The principal investigator of the Sloan-Kettering trials is Bernd Gansbacher, and the brain cancer study is being led by Edward Oldfield of the National Institute of Neurological Disorders and Stroke.

The News & Comment article "New French biomedical center breaks the mold" by Peter Aldhous (25 Sept., p. 1856) neglected to mention the important financial contribution made by the Centre National de la Recherche Scientifique (CNRS) to the Cochin Institute for Molecular Genetics. CNRS provides almost half of the salaries of Cochin Institute personnel and supports one of its major research units.

The price listed for Franco Pavese and Gianfranco Molinar's *Modern Gas-Based Temperature and Pressure Measurements* (Plenum Press) in the Books Received column of 6 November (p. 1015) was incorrect. The price of the book is $110.
