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Testing for fullerenes in geologic materials: Oklo carbonaceous substances, Karelian shungites, Sudbury Black Tuff: Comment and Reply

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Notes

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COMMENT

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The presence of low concentrations of fullerenes has been reported from numerous terrestrial and meteoritic sources (Buseck, 2002). In a recent paper, Mossman et al. (2003) present mass spectra of carbonaceous substances using laser desorption ionization (LDI) and high-resolution electron-impact mass spectrometry. The authors confirm the presence of fullerenes in the Onaping Formation, Black Tuff from Sudbury, Ontario, but do not find fullerenes in carbon-rich shungite rocks from the Lake Onega region of Karelia, Russia. They conclude that the earlier observation of fullerenes in Karelian shungite may have been due to the intrusion of basic igneous rocks and attribute the absence of fullerenes in the four shungite samples they studied to the possible heterogeneity of shungites. However, the authors also argue: ‘‘Alternative explanations include the possibility that fullerenes do not occur in shungite, or that the discovery of fullerenes in shungite may have been an artifact of the analyses’’ (Mossman et al., 2003, p. 257). Moreover, the authors conclude that natural fullerenes appear to form exclusively in extraterrestrial samples. We disagree with these conclusions.

The first discovery of natural fullerenes in a geological sample was reported in shungite from Karelia (Buseck et al., 1992). Ebbesen et al. (1995) speculated that the fullerenes found in shungite were products of a localized event or were due to an experimental artifact; these arguments were challenged by Buseck and Tsipursky (1995). We subsequently reported the presence of fullerenes in shungite samples from Kondopoga (60 km southwest of Shunga), a different locality in Karelia (Parthasarathy et al., 1998). The sample was a bright shungite with ~10 wt% carbon. We used electron-impact ionization mass spectrometer (EIMS) in our experiments for the characterization of fullerenes. In contrast to LDI, which is known to create fullerenes under laser irradiance, EIMS is very safe for detecting fullerenes. The presence of fullerenes in Karelian shungite was confirmed independently by powder X-ray diffraction (XRD) and ^{13}C-nuclear magnetic resonance (NMR) experiments (Parthasarathy et al., 1998). Hence, we do not agree with Mossman et al. (2003) that the fullerenes reported from shungite were due to experimental artifacts.

As has been pointed out by many people, Mossman et al. (2003) among them, Karelian shungite is highly heterogeneous. Fullerenes have only been found in the glassy variety of bright shungite (Buseck et al., 1992; Parthasarathy et al., 1998).

We have carried out a series of experiments exploring the presence of fullerenes in shungite from different areas of Karelia. We present here a typical mass spectra obtained from a dull shungite, in which the total carbon content was estimated to be 60 wt%. Figure 1 shows the mass spectrum of the carbonaceous matter extracted from a dull shungite and exhibits the absence of fullerene. Out of twelve Karelian shungite samples we found fullerenes in only three samples, all of which are bright shungite of glassy nature (Parthasarathy et al., 1998).

There is agreement that natural fullerenes are found in Cretaceous boundary layer samples (Heymann et al., 1994; Parthasarathy et al., 2002), meteorites (Becker et al., 1994), and Permian-Triassic boundary samples (Becker et al., 2001). However, Shimoyama and Yabuta (2002) could not find fullerenes in the Cretaceous-Tertiary boundary sediments at Kawarupu, Japan. We conclude that natural fullerenes exist in Karelian shungite and geological boundary samples. It is the choice of proper sampling that leads to success in finding the natural fullerenes in geological materials. However, the origin of fullerenes in geological materials is not yet understood. Buseck (2002) discussed the occurrence of natural fullerenes in a wide range of geological environments in a comprehensive review, indicating that the fullerenes are not restricted only to extraterrestrial samples. This conclusion is strongly supported not only by our studies on Karelian shungite, but also by the observation of fullerenes in solid bitumen from pillow lavas of Mitov (Jehlic̆ka et al., 2003).

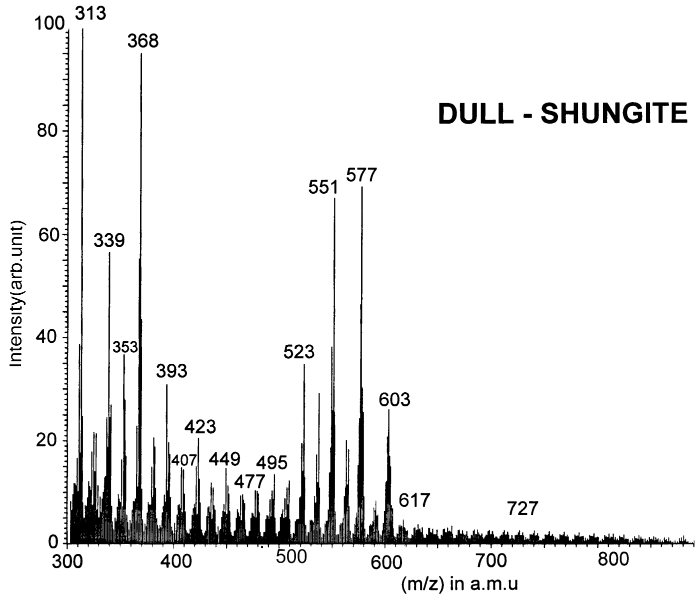

Figure 1. Representative mass spectrum of carbonaceous matter extracted from carbon-rich (60 wt%) dull shungite from Karelia. Please note absence of any peak at 720 atomic mass units (a.m.u.) corresponding to fullerene.

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REPLY

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Buseck et al.'s (1992) discovery of fullerenes in fractures in a shungite sample (enclosed in diabase) from Russian Karelia has been followed by several substantiating reports (see Buseck, 2002, p. 785) as well as by conflicting reports (e.g., Ebbesen et al., 1995; Mossman et al., 2003) concerning the existence of fullerenes in this unusual carbon-rich rock. Thus, Parthasarathy et al. (1998) reported fullerenes in type I (bright) shungites from the Kondopoga mine in Russian Karelia. In light of Mossman et al.'s (2003) failure to find fullerenes in shungite (including type I shungite) from four different localities in Russian Karelia, Parthasarathy and Vairamani's concern certainly seems justified. Is it possible that, after all, fullerenes do not occur in shungite? In his recent review and analysis of geological fullerenes, even Buseck (2002, p. 784) seems convinced that he and his colleagues ''. . . studied an unusual sample.'' But a really unusual sample would have to be the dinosaur eggs reported by Wang et al. (1998) to contain fullerenes! That occurrence might well qualify as a bona fide artifact of the analyses.

As Parthasarathy and Vairamani observe, the sampling problem is crucial. At Kondopoga, the quarry exposes a 500-m-thick lacustrine sequence of graywackes deposited from turbidity currents. This sequence caps ~500 m of basalt overlying the major shungite deposits. Indications are (Filippov, 2002, p. 223–228) that all shungite in the lacustrine sequence is clastic. However it was derived, the Kondopoga clastic shungite has not only necessarily been exposed for an extended interval of time, but it may also represent a residue of basalt-affected lustrous shungite not representative of the usual shungite.

Correction to the comment: we did *not* conclude, as Parthasarathy and Vairamani state, ''. . . that natural fullerenes appear to form exclusively in extraterrestrial samples.'' The word ''almost'' appears in the original (Mossman et al., 2003, p. 258) between the words ''form,'' and ''exclusively.'' A prime terrestrial candidate for natural fullerenes is Jehliĉka et al.'s (2003) confirmation of earlier work (Jehliĉka et al., 2000) reporting the presence of fullerenes in (two of four) samples of solid bitumen enclosed in Proterozoic pillow lavas from Mítov in the Bohemian Massif. Thereby, the likelihood of encountering fullerenes as by-products of contact metamorphism elsewhere is increased—including some shungite from Russian Karelia.

[1]Erratum 25 March 2004: All authors (David Mossman, Guenter Eigendorf, Dennis Tokaryk, François Gauthier-Lafaye, Kristal D. Guckert, Victor Melezhik, Catharine E.G. Farrow) of the original article contributed to this reply and agree with the ideas herein.

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