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

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ABSTRACT

Fullerenes have been reported from diverse geologic environments since their discovery in shungite from Karelian Russia. Our investigation is prompted by the presence of onionskin-like structures in some carbonaceous substances associated with the fossil nuclear fission reactors of Oklo, Gabon. The same series of extractions and the same instrumental techniques, laser desorption ionization and high-resolution mass spectroscopy (electron-impact mass spectroscopy), were employed to test for fullerenes in samples from three different localities: two sites containing putative fullerenes (Sudbury Basin and Russian Karelia) and one new location (Oklo, Gabon). We confirm the presence of fullerenes (C_{60} and C_{70}) in the Black Tuff of the Onaping Formation impact breccia in the Sudbury Basin, but we find no evidence of fullerenes in shungite samples from various locations in Russian Karelia. Analysis of carbonaceous substances associated with the natural nuclear fission reactors of Oklo yields no definitive signals for fullerenes. If fullerenes were produced during sustained nuclear fission at Oklo, then they are present below the detection limit (~100 fmol), or they have destabilized since formation. Contrary to some expectations, geologic occurrences of fullerenes are not commonplace.

Keywords: fullerenes, geologic materials, Oklo, Karelia, Sudbury.

INTRODUCTION

The serendipitous discovery of buckminsterfullerene (Kroto et al., 1985) heralded study of an entirely new series of all-carbon molecules. Then came the first report of fullerenes in geologic materials (Buseck and Tsipursky, 1992), namely in shungite, a highly carbonaceous substance from the village of Shungskoe in the Lake Onega area of Russian Karelia. There, shungite-bearing rocks make up ~70% of the ca. 2 Ga, 650-m-thick Upper Zaonezhskaya Formation, part of a Paleoproterozoic sedimentary-volcanic sequence metamorphosed at low grade (Melezhik et al., 1999). According to Mastalerz et al. (2001), shungite represents in situ organic material that may contain veins of solid bitumen. Fullerenes have since been reported in the interstellar medium (Foing and Ehrenfreund, 1994), and from diverse geologic environments, including fulgurites (Daly et al., 1993), soot from the Cretaceous-Tertiary (K-T) boundary (Heymann et al., 1994a; 1994b), meteorites (Becker et al., 1994a, 2000), meteorite impact sites (di Brozolo et al., 1994; Becker et al., 1994b, 1996), and carbonaceous sediments at the Permian-Triassic boundary (Becker et al., 2001). Fullerenes have also been produced at low pressure in simulations of common flame chemistry (Heymann et al., 1994b; Pope et al., 1993). Ergo, geologic occurrences of fullerenes ought to be commonplace.

Numerous occurrences of shungite lookalikes are associated with the uranium ores and the natural nuclear fission reactors of Oklo. They are currently understood to be various types of solid bitumen or complex carbonaceous substances that served as sources of the bitumens (Nagy et al., 1991; Mossman et al., 1993). Thermally matured to as high as meta-anthracite rank, these organic materials consist of both aromatic (benzenes) and polyaromatic hydrocarbons (including naphthalenes and anthracenes) together with an intimate mixture of cryptocrystalline graphite (Nagy et al., 1993). Transmitted electron microscope (TEM) techniques in a study of optical textures in various types of Oklo carbonaceous substances revealed contrasting ''local molecular orientations'' (Cortial et al., 1990). In some samples, lattice fringe images (see Fig. 1) showed typical onionskin structures characteristic of fullerenes (Ugarte, 1992); this feature prompted the present study.

In the Sudbury basin, strata of the Dowling Member, or so-called Black Tuff, constitute the uppermost of several members of the 1800-m-thick Onaping Formation (Ames et al., 1997). However, they bear little resemblance to shungite. The Onaping Formation is interpreted as allochthonous breccia produced by the meteorite impact that created the Sudbury structure. Added to the complex mixture of fragments of shocked rocks and devitrified glass is ~0.5%–1% organic carbon. Here we report the results of our search for fullerenes in Oklo carbonaceous substances, in Karelian shungite, and in Black Tuff of the Onaping Formation, Sudbury. In this work we used the same series of extractions and the same instruments on samples from the three different localities.

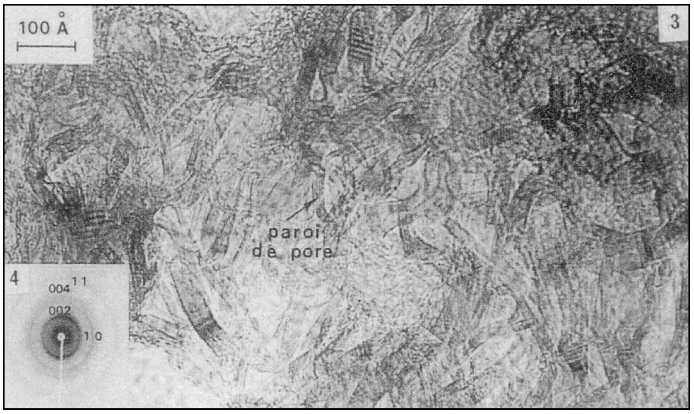

Figure 1. Lattice-fringe image of Oklo sample 8 (previously heated to 2800 °C) reveals onionskin structure and small size of pores and their lack of flattening. Diffraction pattern (lower left) shows diffuse (002) arcs, imparting slight statistical orientation of basic structural units in this organic matter (paroi de pore = partition wall of pore) (after Cortial et al., 1990, p. 79, Plate I, Fig. 3).