



PII S0016-7037(98)00242-7

## Occurrence of natural fullerenes in low grade metamorphosed Proterozoic shungite from Karelia, Russia

G. PARTHASARATHY,<sup>1</sup> R. SRINIVASAN,<sup>1</sup> M. VAIRAMANI,<sup>2</sup> K. RAVIKUMAR,<sup>2</sup> and A. C. KUNWAR<sup>2</sup><sup>1</sup>National Geophysical Research Institute, Hyderabad 500 007, India<sup>2</sup>Indian Institute of Chemical Technology, Hyderabad 500 007, India

(Received March 20, 1998; accepted in revised form July 29, 1998)

**Abstract**—We report on the occurrence of fullerenes in Proterozoic shungite (~2 Ga) from the shungite mine, Kondopoga, Karelia, Russia (62.12°N 34.17°E). The presence of fullerenes has been confirmed by mass spectrometry, with peaks at 360 and 720 amu (atomic mass unit), powder X-ray diffraction showing ten diffraction peaks corresponding to the fullerite structure with  $a = 1.4201(5)$  nm, and <sup>13</sup>C nuclear magnetic resonance (NMR) spectroscopic studies, showing a peak at 143.2 ppm. In the Kondopoga shungite mine, fullerenes occur in silty shales that have experienced greenschist facies metamorphism. Copyright © 1998 Elsevier Science Ltd

### 1. INTRODUCTION

The discovery and synthesis of fullerenes (Kroto et al., 1985; Kroto, 1988) was followed by the discovery of this substance, although rarely, in natural rocks. Buseck et al. (1992) reported their occurrence in ~2 Ga old Precambrian C-rich rocks of Shunga, Russia, called shungite. Other workers found them in rocks that had experienced singular geological events such as lightning strikes (Daly et al., 1993), wild fires at the K-T boundary (Heymann et al., 1994a,b), and meteoritic impact (Becker et al., 1994; Di Brozolo et al., 1994). Since Ebbsen et al. (1995) in their collection of shungites did not find fullerenes, they suspected that the occurrence reported by Buseck et al. (1992) was very localised due to an unusual environmental cause such as a lightning strike. In the absence of evidence for such an environmental cause in the Shunga area of Karelia from which the sample studied by Buseck et al. (1992) is believed to have been collected, and also because of the absence of such evidences in other shungite areas in Karelia, Buseck et al. (1997) contend that shungites are normal greenschist facies metamorphic rocks. We report on fullerenes from shungites of another locality, namely Kondopoga, which should help in substantiating the occurrence of fullerenes in low-grade metamorphic shungites.

### 2. GEOLOGICAL SETTING

The lower Proterozoic sequence of Karelia in Russia is known for its C-rich rocks, referred to as shungite deposits, which have been exploited near Petrozavodsk for the manufacture of light-weight aggregates. The lower Proterozoic rocks of Karelia have been divided into Sumain, Sariolian, Jatulian, Ludicovian, Livvian and, Vespian subgroups. The Ludicovian and Livvian Subgroups are particularly noted for their shungite deposits. Shungite samples for this study were collected from the shungite mine near Kondopoga (Lat. 62.12°N Long 34.17°E, see Fig. 3 in Buseck et al., 1997), located about 60 km southwest of Shunga. The carbonaceous shale belongs to the Suisarian Formation of the Livvian Subgroup, whose age is considered to be ~2 Ga (Sokolov, 1984; Buseck et al., 1997). Our shungite samples are hosted by carbonaceous silty shale at

Kondopoga which exhibits excellent sedimentary structures: rhythmic lamination, graded bedding, ripple marks, mud cracks, sedimentary boudinage, etc. Shatter cones and minerals characteristic of shock metamorphism common in meteorite impact sites are absent. Also there is no evidence for local melting generally associated with lightning strikes. The rock has up to about 10 wt% C. In places, C is concentrated in pockets on the bedding planes. A biogenic origin has been suggested for shungites based on carbon isotopic composition (Borisov, 1956; Volkova and Bogdanova, 1986; Buseck and Valley in Buseck et al., 1997). Silicate veins/veinlets anastomose the C-rich patches. The C portion is pitch black and in parts shows anthracitic sheen, thus resembling the bright shungite (Khoransani and Murchison, 1979). In this respect our samples resemble type I shungites. However, in their low C content and host rock composition they are akin to the characters of the type IV or V shungites (see classification of shungites in Buseck et al., 1997).

### 3. EXPERIMENTAL

The carbonaceous matter was extracted from the shungite sample by using a standard acid-dissolution procedure (Wedeking et al., 1983). The resulting residue was washed with about a liter of distilled water. The washed residue was analyzed by mass spectroscopic, powder X-ray diffraction, and <sup>13</sup>C-NMR spectroscopic methods.

The petrographic studies were carried out on polished thin sections. The electron impact ionization mass spectra were run on a VG AUTOSPEC (Manchester, UK), mass spectrometer with OPUS.V3.IX data system under the following conditions: source temperature, 250°C; electron energy, 70 eV; trap current, 200 μA; resolution, 1000; mass range scanned, 300–900 amu (atomic mass unit); scan speed, 5 s/decade; Interscan delay, 0.5 s. Samples were loaded in a quartz sample cup, introduced through direct inlet probe and instantly heated to 250°C. The mass spectrometer was calibrated up to 900 amu with the reference sample of high-purity perfluorokerosene, obtained from Ms. Fluka, AG, Switzerland. We did not prefer to use synthetic fullerenes as standard so as to avoid any possible contamination of the instrument. The instrument was scanned between 300 and 900 amu to improve the sensitivity of detection of C<sub>60</sub> and C<sub>70</sub>. However, no ions corresponding to C<sub>70</sub><sup>+</sup> could be detected in our samples. Spectra were recorded in a centroid mode. Spectra reported here are an average of 19 scans, though a single scan gives enough signal to identify C<sub>60</sub> fullerene.

Powder X-ray diffraction studies were carried out on the carbonaceous