Geosciences Research, Vol. 1, No. 1, November 2016
https://dx.doi.org/10.22606/gr.2016.11001

Possible Mechanism for the Natural Forming Process of Carbon Nanotubes from Plant Materials

Vladimir V. Chakov[1], Nikolai V. Berdnikov[2] , Alexander P. Kuzmenko[3]
[1] Institute of Water and Ecology Problem, Far East Branch of the Russian Academy of Sciences, Dikopol'tseva St., 56, Khabarovsk, 680000 Russia
[2] Kosygin Institute of Tectonics and Geophysics, Far East Branch of the Russian Academy of Sciences, ul. Kim Yu Chen St., 65, Khabarovsk, 680000 Russia
[3] South-West State University, ul. 50 let Oktyabrya, 94, Kursk, 305040 Russia
Email: `Chakov@ivep.as.khb.ru`

Abstract. The article discusses the results of experimental synthesis of fullerenoids from naturally occurring biogenic materials. Mechanical activation of amorphous carbon derived from Sphagnum moss (*Sphagnum fuscum*) turns it into carbon nanotubes. It is shown that conditions approximating those in the experiment can be generated in settings of active continental margins and intracontinental rifting when lava flows into the basins where sapropels deposited.

Keywords: Sphagnum moss, pyrolysis, carbon nanotubes, mechanical activation, active continental margin, intracontinental rifting.

1 Introduction

The question of the genesis of rocks, which include carbon in the fourth allotropic form, is currently gaining more importance due to the high demand for fullerenes and their derivatives in different spheres of national economy. Versions are presented of both abiogenic and biogenic origins of fullerites, and the same geological and experimental data are often used as evidence [1-5, and others]. The overwhelming bulk of fullerenes, carbon nanotubes (CNTs) and their modifications were found in shungites and their related varieties which are carbon-rich sedimentary rocks that have reached various catagenetic stages [4-8, and others]. In most cases, carbon in this allotrope form is assumed to come from biogenic sources formed by plants and animals [9, 10]. However, graphene and carbon nanotubes were found in natural graphitic globules from igneous rocks [2].

Thus, conditions required for the synthesis of fullerenes and other non-graphite forms of carbon varying from nanotubes to "onion" structures are attainable in geological processes. Experimental reconstruction of such conditions will allow the development of additional physicochemical criteria to search for and to identify geological settings favourable for the formation not only of fullerenes or fullerites, but of other carbon-based skeletal structures of the CNT type. In the very near future, utilization of these experimental approaches will help professionals create environmentally friendly and cost-effective technologies to synthesize novel fibrous materials based on biogenic CNTs.

The formation of high-carbon rocks started in the Proterozoic. At that time, bacteria, phytoplankton and zooplankton, as well as, perhaps, the primitive plant species, such as algae, fungi, lichens and mosses, that occupied the coastal areas of waterlogged soils, accounted for the bulk of the biomass on the planet. Bryophytes were used as a raw material in our experiment to grow carbon nanotubes and fibrous material on their basis.

2 Experimental Procedure

Sphagnum moss (*Sphagnum fuscum*) forms its communities within the boundaries of oligotrophic bogs that are intermediate between upland and aquatic ecosystems. This species of moss has no root system. Precipitation and ground-level condensed moisture almost completely lacking mineral components are the main source of nutrients needed for moss life, hence dewatered phytodetritus of these plants is over

90 percent carbon. Moss samples were harvested from the mire near Lake Kizi (Upper Pleistocene terrace of the Amur River, Khabarovskii krai, 51°35' N, 140°25' E). Moss was additionally carbonized in concentrated solution of the liquid peat phase (the analogue of sodium humate) [11] at the rate of 1 litre per 1 kg of air-dry moss. This procedure also assisted in rendering fractal characteristics to moss samples, which are unique to humic acids [12]. Materials obtained from this kind of raw materials gain the capacity to self-organize and self-assemble [13].

Early in the experiment, the pyrolysis of carbonized sphagnum moss was employed to synthesize amorphous carbon. For this purpose, the moss was cleared from admixtures and dried out in the drying cabinet under the airflow as hot as 45-50°C to have a moister content of 10%. The dry biomass was ground to have a particle size of ≤ 0.5 mm, pyrolyzed in a vacuum furnace (SNVE-2.4.2/16 I2) at 850–950° C for 1-2 hours, and then cooled down to 20°C for at least two hours. At room temperature, the synthesized carbonaceous material has high electrochemical and sorption properties.

Amorphous carbon was mechanically activated in a Pulverisette-4 vario-planetary mill (Fritsch, Germany) in the grinding mode, the speed of the main disc ranging from 200 to 400 rpm and that of the planets from 400 to 800 rpm. In the course of the experiment, 18 balls of 15 mm diameter were used at a wide range of ball-to-powder ratio from 1:50 to 1:250. Milling was efficient at a charge ratio of 1:50 (balls and 10 g of amorphous carbon). Experimentally, it is found that the milling atmosphere (argon, air) has no effect on mechanical activation results.

Mechanical activation of amorphous carbon yielded its nanofibrous modification, i.e., nanotubes between 30 and 40 nm in diameter. The transformation process began in the 7th hour of mechanical activation: no fullerinoids were recorded after 6 hours, by the end of the 8th hour nanotubes accounted for more than 60 percent of the activated material, and after 10 hours almost all the amorphous carbon turned to nanotubes (Fig. 1).

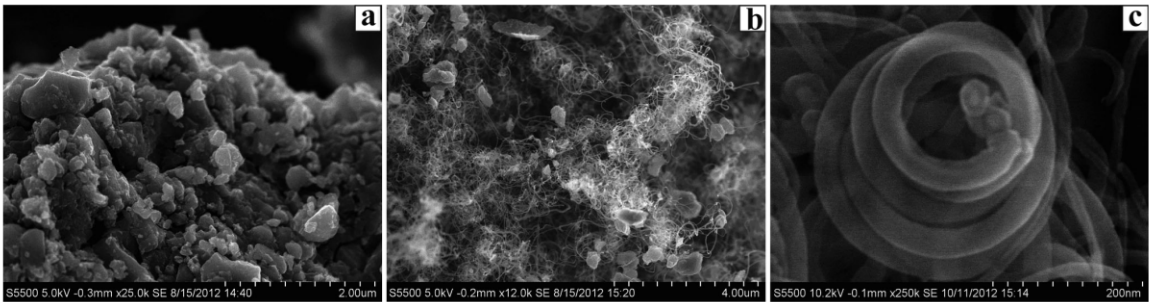

Figure 1. Transformation phases of amorphous organic carbon: a – amorphous carbon from sphagnum moss; b – fibrous material (multi-walled nanotubes) with amorphous carbon particles (8 h mechanical activation); c – multi-walled carbon nanotube (10 h mechanical activation)

The resulting ultrafine particles have large surface areas of 370-550 m^2/g and are characterized by increased chemical activity. Electron microscopy showed that the synthesized CNTs consist of multiple layers of graphene composed of almost pure carbon (Table).

Table 1. Chemical composition of nanocarbon materials after 10 h of mechanical activation

Spectra of analysed points	Content of chemical elements (mass %)							
	O	C	W	Ni	Cu	Co	Fe	Ti
Spectrum 1	0.25	99.1	0.12	0.005	0.007	0.12	0.09	0.017
Spectrum 2	0.24	99.0	0.11	0.004	0.011	0.15	0.07	0.011
Spectrum 3	0.27	99.1	0.10	0.008	0.010	0.14	0.05	0.005
Spectrum 4	0.23	99.2	0.08	0.004	0.009	0.12	0.03	0.029

3 Results and Discussion

Carbon nanotubes production by arc-discharge plasma between two graphite rods is a “classic” version of CNTs synthesis [14, 15]. The process is accompanied by the release of cytotoxic products of high-temperature graphite transformations, which means additional expenditure on preventing their negative impact on the environment. Of the current organogenic carbon-based technologies to produce fullerenes and nanotubes, the most noteworthy technique for their production is through the pyrolysis of acetylene, benzene, methanol and acetone [16, 17, and 18].

Amorphous carbon synthesized from oligotrophic sphagnum mosses by pyrolysis is graphite in its elemental composition. Carbon nanotubes production under mechanical activation of amorphous carbon is less expensive and environmentally friendly. In addition, a renewable raw material (sphagnum moss) is widely available.

The experiment shows that the transformation of amorphous carbon into carbon nanotubes is feasible under the combined action of three main factors: the presence of high-purity amorphous carbon, its pyrolysis in the temperature range of 850-950°C and mechanical activation for a relatively long time. Amorphous carbon in the form of waste products of lower plant-forms has been abundant on the Earth since the early Proterozoic. Its pyrolysis at these temperatures is quite possible, for example, when lava flows into basins during the time of sapropel deposition. Mechanical activation of the generated product can be carried out under friction conditions in the long-lived fault systems.

Additional carbonization of the original plant product is a prerequisite for the process to occur. According to S.I. Zhmur [19], already in the early Proterozoic cyanobacteria started colonizing environments of basins triggering the oxygenation of the Earth’s atmosphere [20]. An increase in the share of oxygen in the atmosphere ensures the synthesis of humic substances in the organic filling of water basins. The presence of carboxyl, hydroxyl and carbonyl groups as well as aromatic compound fragments, makes it possible for humic acids as the most reactive part of humic substances to enter into ionic, donor-acceptor and hydrophobic interactions with organic and mineral materials. This feature is also the characteristic of C_{60} fullerenes that are major constituents of shungites in the *Shunga* and *Zazhogino* deposits [16] whose electron affinity is 2667 ± 0.001 and ionization energy (Ei) is 7.57 ± 0.01 eV. A combination of a much higher electron affinity compared to most organic compounds and low ionization energy indicates the ability of the fullerene molecules to be both as donors and electron acceptors in chemical processes.

In addition, as evidenced by our study, humic substances are capable of self-assembling and self-organizing thanks to the ability to form structural elements of fractal systems [12, 13]. Two-dimensional confocal microscopy showed that the fractal dimension of the pyrolysis product in our experiment is 1.5-1.8. Three-dimensional imaging with a digital holography microscope yielded the fractal dimension of 2.3-2.7 (Fig. 2). As can be seen in the figure, the individual elements of fractal systems are symmetric with respect to the central axis.

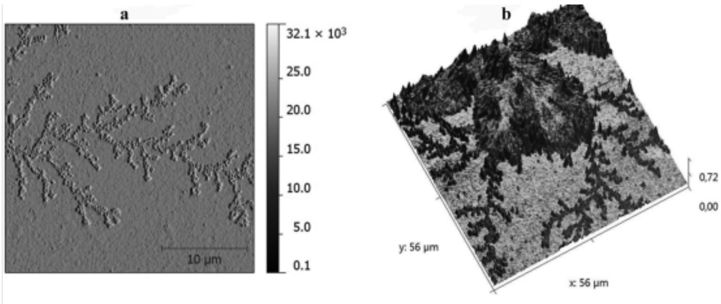

Figure 2. Dendritic architecture of carbon fractals: a – two-dimensional fractal dimensions between 1.5 and 1.8; b – three-dimensional fractal dimensions between 2.3 and 2.7.

Confocal and atomic force microscopy of these fractal systems shows that they are multi-level (Fig. 3) [13].

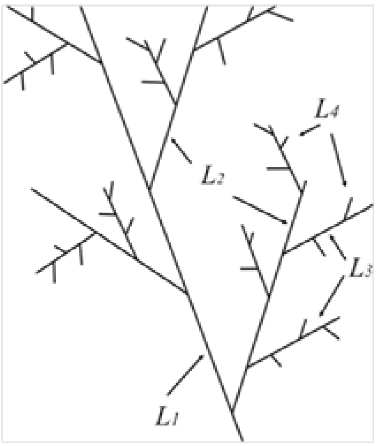

Figure 3. Branches of dendritic fractal schematically.

As seen from the figure, lateral branches of the second order (L_2) develop from the main trunk of the fractal (L_1) in different directions at equal distances to form structural components of lower orders (L_3, L_4, etc.) in compliance with the scheme of monopodial branching. In this case, microscopic imaging with the spatial resolution of 0.5 microns yielded images of branching structures of four orders.

Some researchers believe that the catalytic role of Cu, Pt, Fe, Ni and Co is essential in the formation of carbon nanotubes [21, 22]. In our experiment the catalysts were not used but in nature these elements are present in the eruption products, such as ash, lava and volatiles, and are released in the environment during their cooling.

Thus, we believe that our experiment in the temperature range of 800°C to 1200°C can serve as a model for the carbon nanotubes formation under conditions when lava flows into the basins with sapropel deposits and products of natural pyrolysis further disperse in fault zones. The setting which combines shallow-water basins with zones of volcanic and high tectonic activity is typical of areas of active continental margins and intra-continental rifting. Early Proterozoic deposits of the Onega (pericratonal) and Pechenga (rift) paleobasins of the Baltic Shield studied by A.M. Akhmedov [23] are examples of accumulation and transformation of carbonaceous deposits in settings of this kind, where carbonaceous terrigenous-sedimentary deposits are interbedded with and intruded by basic-ultrabasic lavas, intrusions and tuffs. In the section, there are interbeds and lenses of shungite, as well as shungite xenoclastic lavas, shungite tuffs, vesicular and nodular shungites. Thick sequences are cut into blocks by numerous faults that are mainly normal.

According to A.M. Akhmedov, the formation of high-carbon rocks in these deposits is accounted for by the supply of carbon as a result of volcanogenic-hydrothermal processes followed by its bacterial reduction. Let us analyze geological and geochemical data appearing in his article in the context of the results of our experiment without making any judgments. Geodynamic settings for the formation of deposits in the Onega and Pechenga basins are on the whole consistent with the settings inferred by us, in which naturally occurring fullerenoids can form. The analyses of the relationship between igneous and sedimentary rocks in their sequences and the presence in them of shungite xenoclastic lavas and tuffs are in favour of close high-temperature interaction of volcanic and paleoorganic products. High concentrations of Fe, Co and other elements could provide the catalytic effect during the synthesis of fullerenoids. The isotopic composition of carbon in the rocks studied ($\delta^{13}C_{VPDB}$) ranges from -24.1 to -38.1 ‰ supporting its biogenic nature [24].

Finally, the studied carbonaceous layers are disturbed by numerous faults that could act as a “dispersing agent”. Here the question arises about the locality of the action of these “dispersing agents”. Indeed, the fault zone where rocks are finely ground is in most cases rather thin, so fullerenoids synthesized within it should form narrow bands that mark surfaces of shifting blocks. However, spatial distribution of concentrations of fullerenoids in shungite massifs has not been well understood yet, therefore, it may well be the case. On the other hand, interaction zones of shifting blocks are occasionally thick enough to form zones of mylonite at least one meter wide. For example, M. Finch et al. describe a zone of ultramylonte in NW Argentina as thick as one kilometer [25]. In addition, effects of fractal growth and self-assembly identified in our experiment can be a contributory factor for increasing the area where fullerenoids are synthesized within fault zones. Due to these effects, the area of fullerite fragments growth could expand away from the dispersion centre

We believe that our experiment simulates one of the possible ways for the formation of shungites and fullerenoids contained therein in the natural environment, whereas synthesis of peapods C_{60}@ NT (C_{60} fullerenes inside the nanotubes) suggests an infinite variety of combinations (interpenetrations) of various forms of carbon both with each other and with mineral substances. In most cases, in-depth studies on natural phenomena show that the origin of natural objects can be determined by different processes and/or combinations thereof. A vivid example is the origin of oil, involving most probably both endogenous and exogenous factors in various combinations. The study of these processes offers practical solutions in mineral forecasting and exploration. If our interpretation of the experimental data is correct, then the search for shungites and naturally occurring fullerenoids can be successful in geological settings discussed in this paper.

4 Conclusions

The experiment with organic amorphous carbon demonstrated the feasibility of fullerenoids that are essential for various modifications of 1st class shungite being synthesized under environmental conditions. The presented mechanism for fullerene-like substance synthesis in the temperature range between 800°C and 1200°C (the temperature of lava), which is significantly lower than that of magma, not to mention the temperature of the electric arc plasma at which CNTs are normally synthesized today, indicates not only its cost-effectiveness but also the environmentally friendly production of such materials. The acquisition time chosen (temperature conditions and time frame) is further evidence supporting the organic origin of shungites from sapropel deposits buried under lava flows.

References

1. S. V. Digonsky and V. V. Ten, *The unknown hydrogen.* St. Petersburg: Nauka; 2006. (In *Russian*).
2. V. A. Ponomarchuk, Y. P. Kolmogorov, V. V. Ryabov, A. T. Titov, T. N. Moroz, D. V. Semenova et al., “SR XRF study of natural micro- and nanostructured carbon from igneous rocks”, in *Izvestiya RAN*, *Seriya Fizicheskaya,* vol.77, no. 2, pp. 226–230, 2013. (In *Russian*).
3. V. V. Ryabov, V. A. Ponomarchuk, A. T. Titov and D. V. Semenova, “Carbon micro- and nanostructures in Pt-low-sulfide ores of the Talnakh deposit (Siberian Platform),” in *Doklady Earth Sciences,* vol. 446, no. 2, pp. 556-560, 2012. (In Russian).
4. A. A. Sukhanov, T. K. Bazhenova, E. N. Kotelnikova, “Structural characteristics of a carbonic component of sapropelite kerogen: dependence on the biocoenosis type of the original organic matter and the degree of its catagenesis,” in *Neftegazovaya geologiya*, *Teoriya i praktika,* no. 4, pp. 5-23, 2009. (In *Russian*).
5. M. M. Filippov, “The biogenic hypothesis of the genesis of the Paleoproterozoic metasapropelite,” in *Karelian Research Centre of RAS Trans.,* no.3, pp. 145-156, 2012. (In *Russian*).
6. O. I. Kon’kov, Y. I. Terukov and N. Pfaunder, “Fullerenes in shungite,” in *Fizika tverdogo tela,* vol. 36, no. 10, pp. 3169-3171, 1994. (In *Russian*).
7. P. R. Buseck, S. J. Tsipursky and R. Hettich, “Fullerenes from the geological environments,” in *Science,* vol. 257, no. 5067, pp. 215–217, 1992.
8. P. R. Buseck, “Geological fullerens: review and analysis,” in *Earth and planetary science letters*, no. 203, pp. 781–792, 2002.
9. D. Heymann, L. W. Jenneskens, J. Jehlicka, C. Koper and E. J. Vlietstra, “Biogenic fullerenes?”, *Int. J. of Astrobiology*, vol. 2, no. 3, pp. 179-183, 2003.
10. A. A. Sukhanov, T. K. Bazhenova and E. N. Kotelnikova, “Carbon material of sapropelite kerogen: dependence of structural characteristics on the biocenosis type of the original organic matter and the degree of its catagenesis the biocenotic type of organic matter and the degree of its katagenesis,” in *Geokhimiya*, no. 9, pp. 957–970. 2011. (In *Russian*).
11. D, V. Onishchenko, V. P. Reva and V. V.Chakov, “A method for producing a carbon nanomaterial”, RU Patent 2509053, 2012.

12. V. V. Chakov, N. V. Berdnikov, N. S. Konovalova, “Organic matter of the liquid phase of peat and its hydrolyzates from the deposits of the Middle Amur basin,” in *Russian Journal of Pacific Geology*, vol. 2, no. 6, pp. 553–556, 2008.
13. A. P. Kuzmenko, V. V. Chakov, Nyein Aung Chan, “Controlled self-assembly of micro- and nanostructures,” in *Nanotekhnika*, vol. 4, no. 36, pp. 30–31, 2013. (In *Russian*).
14. M. R. Predtechensky, A. I. Safonov, N. I. Timoshenko, “The Aspects of the history of the rarefied gas dynamics in Russia,” in *History of Science and Engineering*, no. 9, pp. 17-22. 2013. (In *Russian*).
15. E. G. Rakov, *Nanotubes and fullerenes*, Moscow: Logos. 2006. (In *Russian*).
16. V. V. Kovalevski, P. R. Buseck, J. M.Cowley, “Comparison of carbon in shungite rocks to other natural carbons: An X-ray and TEM study,” in *Carbon*, vol. 39, no. 2, pp. 243-256, 2001.
17. V. V. Kovalevski, *Carbonaceous matter of shungites: structure, genesis, classification*, Syktyvkar: IG Komi Science Centre, Doctoral thesis, 2007. (In *Russian*).
18. J. Deng, Y. You, V. Sahajwalla, R. K. Joshi, “Transforming waste into carbon-based nanomaterials,” in *Carbon*, no. 96, pp. 105–115, 2016.
19. S. I. Zhmur, *The role of cyanobacteria in the formation of high-carbon rocks*, Moscow: KomKniga, 2010. (In *Russian*).
20. I. R. Klesment, Y. B. Bondar, “The biochemical aspects of sapropelite evolution according to molecular paleontology,” in *Goryuchie slantsy*, vol. 5, no. 2, pp. 129–146, 1988. (In *Russian*).
21. R. T. R. Baker, “Catalytic growth of carbon filaments,” in *Carbon*, vol. 27, no. 3, pp. 315–323, 1989.
22. K. Moothi, S. E. Iyuke, M. Meyyappan and R. Falkon, “Coal as a carbon source for carbon nanotube synthesis,” in *Carbon*, vol. 50, no. 8, pp. 2679–2690, 2012.
23. A. M. Akhmedov, “Closed metalliferous carbon-accumulating systems in the Early Proterozoic volcanogenic-sedimentary basins of the Baltic Shield,” in *Regionalnaya geologia i metallogenia*, no. 4, pp. 122–135, 1995. (In *Russian*).
24. H. R. Rollinson, *Using geochemical data: evaluation, presentation, interpretation*, Essex: London Group UK Ltd., 1994.
25. M. A. Finch, R. F. Weinberg, M. G. Fuentes, P. Hasalová, R. Becchio, “One kilometre-thick ultramylonite, Sierra de Quilmes, Sierras Pampeanas, NW Argentina,” in *J. of Structural Geology*, no. 72, pp. 33–54, 2015.