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Genesis of Karelian Shungite with Reference to Its Distinctive Structural Features[1]

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Abstract—Structural data on shungite-bearing rocks were used to develop a new model for their nanostructure and the natural processes of their genesis and evolution. A conclusion was made that the natural solid carbon of shungite is composed of carbon black particles in a fossilized tarlike hydrocarbon matrix. Both were produced by the burning of deep-seated methane in oxygen-deficient environments. The total amount of the burned-out gas was assayed at 10×10^9 t. The gas escape was accompanied by hydrotherms with other compounds, which produced the mineral components of shungite rocks. It is hypothesized that shungite may be underlain by rocks containing hydrocarbons, which were preserved, in a certain form, to the present.

INTRODUCTION

The genesis of unique deposits of solid carbon in the Lower Proterozoic (Ludorikian and Kalevian) shungite rocks in Karelia is a matter of long-lasting discussions. Although the problem was attacked in several papers and monographs [1–6] and detailed data are currently available on the geology of the deposits and the main physicochemical properties, composition, and textures of shungite rocks, no consensus concerning their genesis has yet been attained. Modern hypotheses dealing with the origin of these rocks can be grouped into two categories: biogenic and abiogenic. According to the former, shungite carbon was provided by bacteria and protists (single-cell algae), whose organic matter (OM) may have given rise to, for example, the oldest black shales. Shungite rocks could result from deep metamorphism of these rocks. The proponents of the other group of hypotheses believe that the source of shungite carbon was organic silicate complexes, hydrothermal solutions, juvenile carbon dioxide, and/or hydrocarbons (HC) of abiologic genesis. These were transported to the surface by active volcanic processes, which were typical of that time, and produced shungite deposits when protoshungite matter was somehow transformed into sediment.

In this paper, I attempted to attack the problem of the genesis of shungite carbon based on data on its nanostructure.

STRUCTURE OF SHUNGITE CARBON

For definiteness sake, let us define shungite or shungite matter as carbon that is contained, along with mineral components, in shungite rocks.

The structure of shungite rocks is made up of an amorphous conductive matrix with equally distributed grains of silicates and other compounds [4]. The rocks have well-developed microporosity, a system of channels along which decomposition products of the parental matter are evacuated. The pores range between 10 and 28 Å in width and are mostly of the closed type [2]. Several shungite properties, including its external appearance, resemble the properties of synthetic glassy carbon.

In accordance with the weight concentration of solid carbon, C_s, the rocks are conventionally classified into five varieties [4–6]: $C_s < 10\%$ for variety V, 10–20% for variety IV, 20–35% for variety III, 35–80% for variety II, 95–98% for shungite I, which is, thus, nearly pure shungite matter. Shungite I mainly occurs in veins and, more rarely, lenses, which range from a few to a few dozen centimeters in thickness.

Electron microscopic results [7] definitely indicate that a typical supramolecular particle of shungite carbon is a globule, a spherical particle whose diameter L does not exceed 100 Å (Fig. 1). The coherent X-ray scattering regions (CXRSR) are microcrystallites composed of L_c = 3–6 graphite-like layers. As follows L_a from their electron diffraction patterns [4] and Raman spectra [8], the microcrystallites are as large as ~25 Å. They are defective and strongly distorted. Their typical spacing is $d \approx 3.5$ Å, i.e., much larger than $d_{002} = 3.355$ Å of crystalline graphite. It is commonly believed that CXRSR are the flattest areas of the shell of a globule, which is supposedly hollow. Globules generally occur

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[1] By publishing the paper by V.I. Berezkin, the editorial board is aware that many aspects of the concept developed in it are inconsistent with the actual geology of Karelian shungite-bearing rocks. However, the complexity and uncertainty of the genesis of these rocks justifies search for alternative ideas.

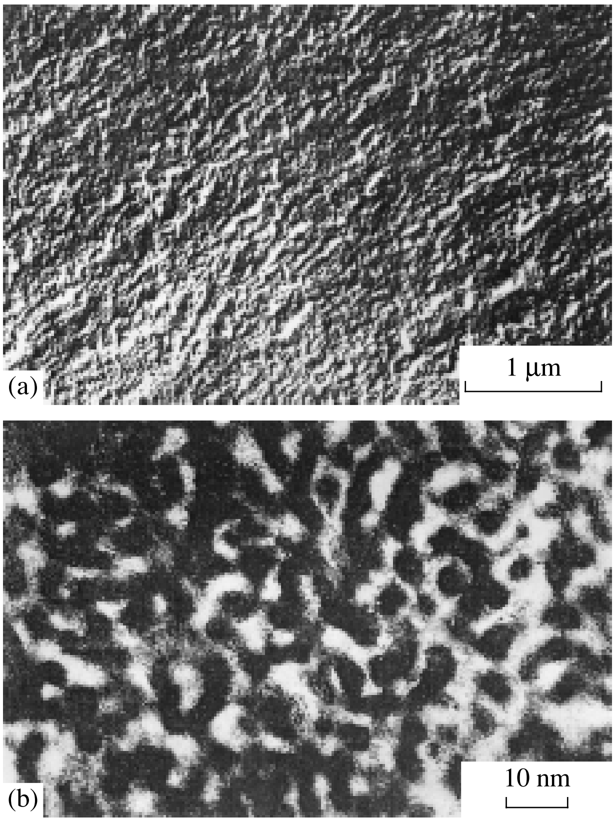

Fig. 1. (a) Morphological structure of globular shungitic carbon cleavage split. (b) Transmission electron microscopic image of a thin cleavage split of shungitic carbon. Arrows point to globules [5].

in physical contact with one another, with the interstitial space filled with carbon that does not form any regular network and maintains bonds between globules. This type of close packing explains, first, why the highly porous shungite matter is practically impermeable to gas and, second, why the density of natural shungite carbon varies from 1.79 to 1.98 g/cm^3 [1, 4]; i.e., why it is of the order of high-grade artificial graphite and much higher than the density of synthetic glassy carbon (1.4–1.5 g/cm^3, [9]), which has a principally different structure [10]. The globular nature of the shungite structure and the close packing of its globules are also directly confirmed by tunneling microscopy [11] and, indirectly, by the conductivity of shungite matter. The latter is very high (2.9×10^2 Ω^{-1} cm^{-1}) and is only one order of magnitude lower (due to the scatter of charge carriers at globule boundaries [12]) than the conductivity of single-crystal graphite in the direction of its carbon planes. The globular structure of shungite matter explains its high resistibility to graphitization [13].

The diversity of shungite structures can be reduced to a few types [5]. Globular shungite (Fig. 2a) consists of spherical globules with $L \approx 60$–100 Å, a wall thickness of $L_c \approx 17$–18 Å, an inside pore 30–60 Å in diameter, and a characteristic CXRSR length of $L_a \approx 25$ Å.

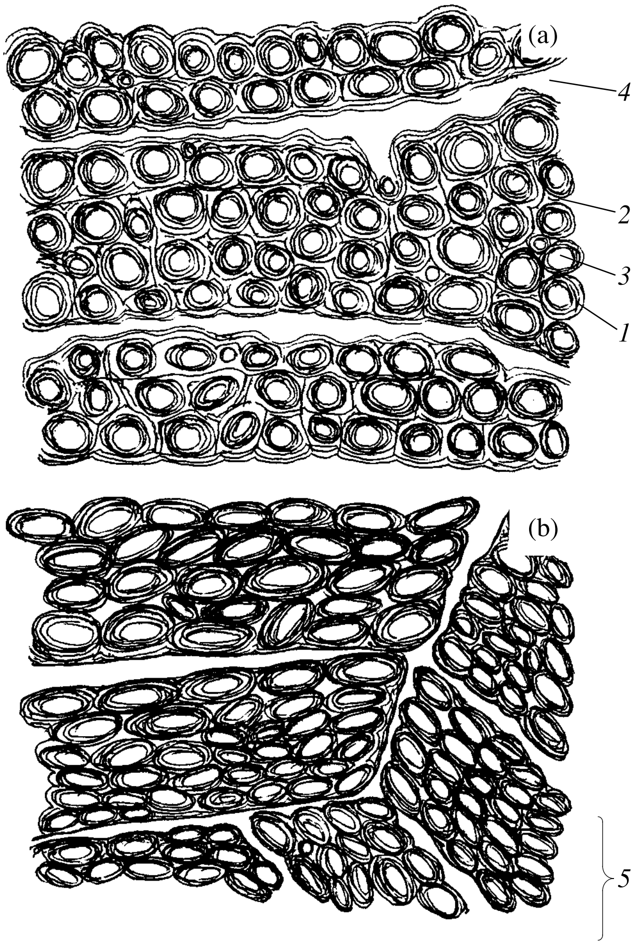

Fig. 2. Model for the structure of shungite matter with (a) spherical and (b) elliptical globules.

(*1*) Globule; (*2*) interstitial carbon; (*3*) inner pore of a globule; (*4*) outer interstitial pore; (*5*) globular layer [14].

Globules are submerged in carbon, which has relatively weak chemical bonds and can be readily oxidized during chemical treatments. The latter process results in the segregation of individual globules and their clusters. Spherical globules compose layers ~400 Å in thickness and up to 10 μm in length [14]. The layered (Fig. 2b) structure typically has flattened ellipsoidal globules ($L_a \approx 35$ Å) with a mutual definite orientation of globules within layers (~2000 Å in thickness). The layers compose stacks up to 2–4 μm long. The globules are relatively strongly mechanically bound with one another, and the layers of globular and layered structures are separated by external interglobular pores. Flaky shungite ($L_a \approx 60$ Å) consists of strongly flattened globules with the smallest internal pores. They are strongly bound with one another and are often mechanically indistinct. Globules compose clusters in the form of flakes up to 1 μm with uniform anisotropy. The film structure is characterized by the absence of internal pores ($L_a \approx 70$ Å, $L_c \approx 34$ Å), clearly distinct globules, and crystallographically differently oriented CXRSR, which result in clearly pronounced anisotropy. The film mode of shungite occurrence consists of thin (200–500 Å) sheets up to 50 μm long on the faces of large crystals.

There is a correlation between the geological setting of shungite within layers and its structure. In drill holes with insignificant temperature gradients and nearly normal pressure, the globules are spherical and the interglobular porosity may be as high as 24%. Where the pressure is higher, massive nucleation of layered structures was noted, along with a decrease in the interglobular porosity to 5.5% [14]. Shungite matter with a layered structure displays a lower percentage of carbon that does not belong to any regular network than in globular shungite. The interlayer and intralayer distortion decreases from spherical globules to films. Simultaneously, d also decreases, for example, from 3.53 Å (depth 0 m) to 3.50 Å (depth 40 m) and 3.42 Å (depth 70 m). It is worth mentioning that globules have a uniform size, a fact testifying to the uniform processes and conditions that brought about shungite rocks. It is commonly thought that they were produced under relatively mild conditions [4]. According to other notions, the temperatures at which the primary OM was transformed were no lower than 300–400°C [15] or even 600–700°C [16], and the pressure attained was 7 MPa [17].

The occurrence of globules is also typical of black shales. Globules and micelles were found (although in smaller amounts) in coals [18]. The difference of the structures of shungite matter from the turbostratic structure of black shales and coals is the fact that globules are the main genetic feature of shungite.

It was proposed [18] that globules cannot be produced by any “normal” metamorphic process in carbon deposits of any type. Such a process was described as follows in [5]. First, long molecules of chain-forming HC in shungite matter form balls to minimize their internal energy and, later, are carbonized under mild conditions over a long time period. The gaseous byproducts diffuse outward and inward and form, in the latter case, a close pore. A variety of factors eventually lead flattened globules to be bound into stacks of layers.

This mechanism of globule genesis seems to put forth more problems than provide answers and solutions. For example, it remains unclear as to which conditions could result in a strong graphite-like shell and where the carbon from the ball interiors was removed (to give place to the inner pore). Furthermore, it remains obscure as to how the strong interglobular bounds could be created and which process forces the molecules to form balls. Indeed, there is a great variety of organic compounds with very long, but nevertheless linear, molecules. Finally, nothing is known on the precursor of the protoshungite matter. If it were of organic genesis, it could have been only proteins whose macromolecules of the third and fourth orders of morphological organization may have the shapes of balls or their clusters [19]. It is easy to calculate that a 100-Å shungite globule consists of roughly 10^5 carbon atoms, which correspond to the heaviest protein molecules or their aggregates. However, it is very hard to envision shungite matter as slightly transformed (outer shell and inner pore), carbonized, and closely packed ancient protein molecules.

However, in my opinion, it is realistic to hypothesize, in accordance with this model, that the same mechanism could be responsible for the balling of carbon clusters into fullerene molecules, C_{60} and C_{70} (which were found in shungite [20]), and the origin of the globules. The latter seem to be nothing else but carbon black particles.

Primary carbon black particles are spherical globules. The X-ray diffraction patterns are similar for cinder black and shungite matter. The typical CXRSR of, for example, furnace black is characterized by the following parameters: $d = 3.55$ Å, $L_a = 36$ Å, and $L_c = 22$ Å (i.e., six graphite-like layers) [21]. The density of carbon black, 1.8–2.0 g/cm^3 [22], is the same as the shungite matter density. The chemical composition of shungite matter [1, 6] is practically identical to the chemistry of carbon black [23]. When the latter is produced using HC in the presence of catalysts [17] (such as aqueous solutions of Mg, Ca, Mn, Cu, Fe, Co, Ni, and other salts), some of the resultant structures are similar to those in shungite. These are, for example, long carbon fibers with several links, which are sometimes interpreted as fossil seaweed. Furthermore, shungite deposits often contain sooty varieties of shungite matter, which fills in cavities in rocks [6]. Loose sooty shungite material was also found in the form of massive carbonaceous tuff beds [5]. Disseminated shungite matter in high-ash rocks consists of globules whose size, morphostructure, and secondary structure are identical with those of carbon black [1]. Finally, the rocks themselves leave a black, sooty streak, and varieties II and III are very high in ash.

GENESIS OF GLOBULAR BLACK CARBON PARTICLES

Widely used dispersed solid carbon (carbon black) is usually the product of thermal decomposition of HC during their incomplete combustion (under oxygen-deficient conditions) or pyrolysis (in oxygen-free environments). Carbon black, an important type of feedstock, may be obtained in production quantity by a variety of techniques with the use of liquid or gaseous HC within the temperature range of 1150–1400°C. Individual particles of carbon black vary from 90 to 6000 Å in size [24] and are either individual globules or their aggregates in the form of branching linear chains, fibers, spirals, bunches, etc. The fast development of carbon black particles is a complex process, and many details of its molecular-scale mechanism remain unclear as of yet. This is partly accounted for by the lack of data on intermediate decomposition products, particularly at temperatures of 1000°C and above. Scarce data are available only on the simplest HC. For instance, chromatograms of methane pyrolysis (Fig. 3) suggest the origin of several intermediate HC (including liquid HC) and significant amounts of H_2 and O_2. The final products are dominated by naphthalene, $C_{10}H_8$, and anthracene, $C_{14}H_{10}$ [26], i.e., compounds that are solid under normal conditions. Technologically, carbon black can be classified into channel black, furnace black, and thermal black [23].

Channel black is produced in a laminar flow in smoky diffusion flames. The carbon black yield with the use of gaseous HC varies from 10% (of the initial carbon concentration in the gas) to 20% (when benzine HC are used). Because of the rapid passage of the HC flow through the reaction volume, the globules stop growing upon attaining L = 90–290 Å, and their secondary structures (aggregates) are only poorly developed. The finest grain carbon black is produced from methane (the yield is 1–1.5% [27]). The carbon black flow during its combustion is accompanied by a flow of pitchy compounds (oily dark brown HC with a melting point of ~100°C), which are sorbed by carbon black particles and reaction chamber walls and whose amounts may be two times that of the carbon black [28]. These compounds deteriorate the carbon black quality, and, thus, precautions are taken to eliminate them from the products. Similar to aqueous suspensions of shungitic carbon, those of channel black have pH 3–5 (the pH of furnace and thermal black is 8.0–9.5 [24]). This is explained by the high concentration of oxygen-bearing radicals (hydroxyl, carbonyl, etc.) at the surface of the particles, which make them easily wettable by liquid (oleophilic) HC.

In contrast to channel black, furnace black is produced in a diffusion turbulent flow. The turbulent character of the flow is usually attained by introducing the feedstock in a direction perpendicular to the combusted gas flow. In spite of the high (up to ultrasonic [21]) velocities of the introduced HC during the furnace process, the decomposition products remain within the high-temperature zone for a longer time than during the channel process, and, hence, the average particle sizes vary from 180 to 900 Å [24]. The carbon black yield may become as high as 60%, and liquid HC can sometimes be produced under certain conditions.

Thermal black is produced by HC pyrolysis in the absence of oxygen, with the yield of carbon black attaining 90–95% [23]. The average size of particles covers the interval of 1800–4700 Å [24]. In thermal black production, the burning of combustible gas heats the furnace to 1300–1600°C, the addition of oxygen is then stopped, and the same gas is subjected to pyrolysis. As the temperature decreases to ~1200°C, the heating is resumed. Methane thermal decomposition may often be coupled with carbon black contamination with significant amounts of pitchy products.

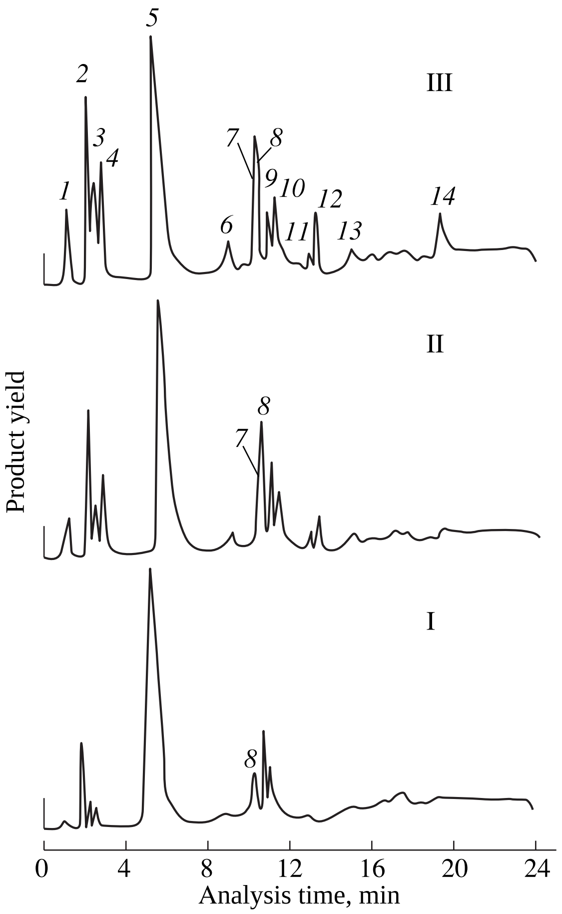

Fig. 3. Chromatograms of gas during methane pyrolysis. The hot surface temperature is 1250°C, initial pressure is 7 kPa (50 mm Hg).

Curves: (I) 1.5 h after the beginning of the process, (II) same, after 4.5 h, (III) same, after 7.5 h. (*1*) H_2; (*2*) N_2; (*3*) O_2; (*4*) CO; (*5*) CH_4; (*6*) CO_2; (*7*) C_2H_2; (*8*) C_2H_4; (*9*) C_2H_6; (*10*) H_2O; (*11*) C_3H_6; (*12*) C_3H_8; (*13*) HC with C_4; (*14*) C_6H_6 [25].

The characteristics of carbon black material depend on technological conditions [23]. With an increase in the molecular weight of the feedstock, the carbon black yield increases and its grain size decreases. To obtain poorly structured fine-grained carbon black, the feedstock oxygen concentration is increased (to increase the temperature of the process), or hydrogen is additionally introduced in order to produce a protective layer at the surface of particles to inhibit their growth and aggregation. The same goal can be achieved by the introduction of catalysts (in the form of alkalis or alkali salts), whose sufficient amounts do not exceed ~100 g per ton of feedstock. The size of carbon black particles can be decreased by diminishing the concentration of input liquid or gaseous feedstock by its dilution with, for example, nitrogen. The concentration levels (below which no carbon black is produced) are therewith 63 vol % methane at 1000°C or 2.8% at 1200°C [27]; i.e., the dilution may be very significant.

Fullerenes are commonly considered to be a variety of carbon black particles [29]. In incomplete combustion of gaseous HC, in particular, at flow velocities of 25–50 m/s and a combustion temperature of ~1700°C, the yield of fullerenes is ~10% of the total amount of produced carbon black [30]. As a consequence of the spontaneous condensation of the HC decomposition products, fullerenes occur in all smoky flame types. It is generally believed [31] that any appreciable amounts of fullerenes can be obtained from the flame of an ordinary paraffin or stearin candle. There are no principal differences between the production technologies of fullerenes and carbon black, and the only problems concern the efficiency of certain techniques and the structures that can be produced by them. Fullerenes were hypothesized [32] to serve as the cores of carbon black balls; i.e., both carbon types should be related genetically.

GENESIS OF SHUNGITE ROCKS

The nanostructure of shungite matter considered above and the processes resulting in closed globular carbon particles led us to put forth the following hypothesis [33].

Shungite deposits were produced by the combustion of primary HC in oxygen-deficient environments. The HC was mainly methane, because its combustion yields the finest grained carbon black, and this gas is contained in vast amounts in the Earth’s interiors. Volcanic activity created vertical pathways and discharge zones, to which deep-seated flows were directed. HC were combusted under high pressures and temperatures. CH_4 is known to spontaneously ignite in the presence of O_2 at temperatures as low as 360–400°C under normal pressure [27], and, as the pressure increases, the temperature of methane spontaneous ignition decreases, so that it ignites at a temperature of 200°C at a pressure of 5 atm. High temperatures and pressures and a deficit of oxygen during the origin of shungite rocks are confirmed by the occurrence of traces of crystalline carbon (diamond and graphite) in them [34]. These processes were associated with relatively active resinification, a process inherent in the thermal transformation of methane. Consequently, viscous mobile masses of resin-covered carbon-black particles were produced, which migrated along cracks and faults that are intercalated with the host rocks, were forced to the peripheries of productive horizons, or spread on the surface.

Given the overall reserves of the deposit, the low carbon black yield during methane combustion, the extremely small sizes of globules in the succession of carbon black particles, and the fact that the secondary structure of stable aggregates is atypical of shungite, it can be theorized that the combustion processes were long-lasting and may have been coupled with all conditions favorable for the smallest size of carbon-black particles. In other words, these combustion processes may have proceed at high velocities of HC flows, high (>1000°C) combustion temperatures, at the dilution of the HC feedstock, and in the presence of large hydrogen amounts and catalysts.

If the diluents and catalysts were transported predominantly in the form of accompanying hydrothermal flows, this may explain the homogeneity of mixing between the rock components. The hydrotherms may also have served as a source of O_2 and H_2 in the form of water steam, which was decomposed under high pressures and temperatures. It is known [19] that the thermal dissociation of water starts, at normal pressure, at ~1000°C but may decrease even to 100°C in the presence of catalysts.

It seems to be mainly the dilution of HC that determined the weight proportions of the shungite matter and mineral components. As was mentioned above, the C_s concentration of shungite rocks does not exceed 80%. If the main dilutant was hydrotherms, whose mineralization was approximately 10 g/l, then, taking into account the efficiency of carbon black production from methane, the amounts of hydrothermal solution participating in the formation of shungite rocks may be estimated at ~20% of the amounts of methane. Shungite I, whose concentrations in the rocks are extremely low, seems to result from the local segregation of carbon and rock or their poor initial mixing.

By the beginning of the next stage, the protoshungite matter consisted of globules whose interstices were fully filled with cementing material. This created prerequisites for the development of massive rocks with a low permeability to gas. The matrix material was present in sufficient amounts, or else porous structures were produced [35]. With the passage of time, the cementing material was polymerized and gradually carbonized. Chemical bonds between carbon atoms in the globules and macromolecules of the cementing matrix became stronger, the diffusion of unbound electrons increased, and strong covalent bonds were formed because of the overlap of electron orbits and exchange interaction of π electrons. The spin states were delocalized and, through-conductivity, developed. These processes should have been associated with, for example, a significant increase in the conductivity and a decrease in the relaxation time of the spins of interacting paramagnetic centers. This effect can be observed when composites of carbon black with cementing HC are thermally treated [36, 37].

The evolution of shungite rocks depended on the rock pressure. Where it was not very high, the bonds between the globules and matrix were weaker. In higher pressure environments, globules occurred in closer contact with one another, became deformed, and the excess material was squeezed out. Consequently, the percentage of disordered carbon decreased and that of elliptical globules increased. These globules are strongly connected with one another and may sometimes become undistinguishable. It was impossible to transform protoshungite matter into massive rocks in the absence of matrix HC, because, as is well known, dispersed carbon black cannot be compacted without certain additives.

Membranous shungite could be produced by metamorphism of heavy HC layers on the surface of crystalline rocks. Part of these HC, which was not mixed with carbon black masses, may have given rise to bitumen, which were found in significant amounts near shungite deposits [5].

Hence, if shungite matter is an assemblage of carbon black with fossilized cementing HC, it is quite natural that they carry fullerenes. At the same time, it is understandable why their concentrations are as low as 0.01–0.10% in rocks of type III [38]. It is very hard to derive any significant amounts of these compounds from dense massive material, whose hardness is the same as the hardness of glass.

CONCLUSION

The hypothesis discussed in this paper readily explains why numerous attempts to utilize shungitic carbon as a fuel were doomed to failure. Indeed, shungitic matter is, in a sense, “combusted,” although not oxidized to CO and CO_2.

The unusual structure of shungites justifies their recognition as a specific type of solid carbon. In my opinion, the viewpoint that they are strongly metamorphosed black shales is not correct. It is sometimes believed that the fact that shungite cannot be graphitized is explained by its structural “memory” of the sapropel-related genesis of shungite matter, whereas this property of shungite is, in fact, caused by its globular structure. In this connection, it is pertinent to mention that fine-grained carbon black is also not graphitized, and, if it actually consists of globules, the latter do not change their morphology up to the temperature of carbon sublimation. The occurrence of globules in black shales and coals might be caused by high-temperature processes (explosions, combustion, or pyrolysis) within certain layers. Similarly to long-lasting underground fires in peat beds, these processes occur far from rarely.

Shungite rocks are monogenic, because, in my opinion, they were formed by a single process of the discharge of juvenile hydrocarbon-bearing fluids within a relatively small area. If the age of the rocks is ~2 Ga, the original HC fuel should be even older, since it is hard to envision simultaneously occurring processes of HC formation and combustion in significant amounts.

The genesis of the parental deep-seated methane can be refined when the probable scale of biological activity in Karelia during the Early Proterozoic, or even earlier, is clarified, because, according to [11], shungite rocks occur even in the Archean. For this purpose, it is necessary to determine whether hydrobionts could produce billions of tons of parental OM matter within the relatively small Lake Onega area during this time. It should be taken into consideration that oil and gas yields do not exceed one-fifth of the mass of the parental biogenic OM [39], and the total estimated reserves of shungite rocks are as high as 600×10^9 t [40]. If the answer is negative, it should be admitted that shungite rocks are of endogenic genesis. At the same time, if biogenic OM was available during the development of the deposits, it could be involved in shungite production and mixed with the protoshungite matter. Finally, some inclusions that are found in shungite and definitely classed with fossilized remnants of microorganisms may have been formed in the shungite matter later, in connection with the development of a nutrient medium in the form of compounds synthesized from, for example, formaldehyde, CH_2O, which is one of the products of incomplete methane oxidation or may be readily synthesized from mixtures of CO, CO_2, and H_2 or CH_4 and O_2. These compounds could be urotropin, carbamid, formic acid, methanole, sugars, which are widely used in organic synthesis, etc. One-cell organisms utilize synthetic HC on the basis of CH_2O even if it is the only nutrition source [41]. It was noted in [1] that, if the parent shungite matter served as a nutrient medium for ancient microorganisms, their concentration was not high and they could rework merely insignificant parts of the original material.

Provided the mass of shungitic carbon is $\sim 100 \times 10^6$ t and the efficiency of soot formation equals ~1%, the amount of combusted HC feedstock was of the order of 10×10^9 t, which can be regarded as the lower limit if the origin of resins is taken into account. To put it otherwise, another unique feature of shungite rocks is the fact that natural stable conditions were created that were favorable for long-lasting oxygen-deficient combustion of vast (even in accordance with the roughest estimates) HC amounts. In this context, one of the causes of the development of a syncline, whose shallow depression hosts shungite deposits, might be the escape of deep-seated methane. Moreover, it seems to be possible that, on the one hand, not all methane was combusted, and, on the other, part of the resultant heavy HC remains conserved beneath the shungite until now. Hence, it makes sense to examine the Lake Onega area for the presence of HC, particularly considering the fact that no such works have ever been conducted in the area.

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