Shungite as the natural pantry of nanoscale reduced graphene oxide

Elena F. Sheka\textsuperscript{a,*} and Natalia N. Rozhkova\textsuperscript{b}

\textsuperscript{a}General Physics Department, Peoples' Friendship University of Russia, Moscow 117198, Russian Federation, \textsuperscript{b}Institute of Geology, Karelian Research Centre RAS, Petrozavodsk, Russian Federation

(Received 19 November 2013; final version received 17 January 2014)

Shungite is presented as a natural carbon allotrope of a multilevel fractal structure that is formed by a successive aggregation of \(\sim 1\) nm reduced graphene oxide nanosheets. Turbostratic stacks of the sheets of \(\sim 1.5\) nm in thickness and globular composition of the stacks of \(\sim 6\) nm in size determine the secondary and tertiary levels of the structure. Aggregates of globules of tens of nanometers complete the structure. Molecular theory of graphene oxide, supported by large experience gained by the modern graphene science, has led to the foundation of the suggested presentation. The microscopic view has found a definite confirmation when analyzing the available empirical appearance of shungite. To our knowledge, this is the first time a geological process is described at quantum level.

\textbf{Keywords:} shungite; reduced graphene oxide; molecular theory

1. Introduction

Carbon is an undisputed favorite of Nature that has been working on it for billions of years thus creating a number of natural carbon allotropes. Representatively, we know nowadays diamond, graphite, amorphous carbon (coal and soot), and lonsdaleite. For the last three decades, the allotrope list has been expanded over artificially made species such as fullerenes, single-walled and multi-walled carbon nanotubes, glassy carbon, linear acetylenic carbon, and carbon foam. The list should be completed by nanodiamonds and nanographites as well as one-layer and multi-layer graphenes. Evidently, one-to-few carbon layers adsorbed on different surfaces should be attributed to this cohort as well.

In spite of high abundance of the carbon allotropes, the above list remains incomplete until shungite is added to the group of natural allotropes. As has been known, this natural carbon deposit cannot be attributed to either diamond, or graphite and amorphous carbon. A lot of efforts have been undertaken to exhibit that the material, once pure carbon by content, presents a fractal structure of agglomerates consisting of nanosize globules [1], each of which presents a cluster of \(\sim 1\) nm graphene-like sheets [2]. The current article presents a summarized view on shungite as carbon allotrope and suggests a microscopic vision of the shungite derivation supplemented by the presentation of its structure as a multistage fractal net of reduced graphene oxide (rGO) nanosheets.

\*Corresponding author. Email: sheka@icp.ac.ru

© 2014 The Author(s). Published by Taylor & Francis.

This is an open-access article distributed under the terms of the Creative Commons Attribution License http://creativecommons.org/licenses/by/3.0/, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited. The moral rights of the named author(s) have been asserted.
2. Shungite as we know it

Shungite rocks are widely known and are in a large consumer’s demand due to its unique physicochemical [3] and biomedical properties [4]. For a long period, thorough and systematic studies, aimed at clarification of the reasons of such uniqueness, have been performing. As has been gained [1], shungite carbon of natural deposits is a densely packed porous structure of agglomerates with a large variety of pore size from units to hundreds nanometer. Such a large dispersion of the pore size evidences a multistage structure of agglomerates that points to the fractal accommodation [5]. The shungite fractal structure has been clearly evidenced by small angle neutron scattering (SANS) [6] that showed two types of shungite pores, namely, small pores with linear dimensions of 2–10 nm and large pores of more than 100 nm in size. The findings allowed suggesting that the shungite fractal structure is provided with aggregates of globular particles of ~6 nm in average size. Within the framework of the first ideas in the 90s, the globules were seen as fullerene-like structures [7]. However, thorough studies, particularly, high-resolution electron microscopy, X-Ray diffraction, and Raman scattering showed that the globules are clusters (stacks) of graphene-based fragments of ≤1 nm in size [8,9]. X-ray [3] and neutron [8] diffraction showed the graphite-like packing of the latter characterized by the interfacial distance of 3.40(3) Å [3] and 3.50(3) Å [10]. The length of the coherent scattering region along c-axis constitutes 2.2(1) nm [3] and 1.5(4) nm [10]. The data show that shungite globules present aggregates of six- and five-layered graphene-like stacks.

As has often been observed [11], solid fractals have increased solubility with respect to dense solids. In full accordance with this, shungite can be quite easily dispersed in water in contrast to solid fullerenes, nanographites, and other sp² nanocarbons. Shungite aqueous dispersions, with maximum achieved concentration of ~0.1 mg/ml, are described in details elsewhere [1,8]. If the water evaporation is blocked, the dispersions are quite stable and conserve properties during a long period of time (for several years). A complete drying of the dispersions results in the formation of densely packed powdered colloid condensate. The structural and physicochemical characteristics of the latter are similar to those of the pristine shungite [9].

The close link between the pristine shungite, its aqueous dispersions, and the condensate is clearly visible through Raman scattering. Figure 1 shows Raman spectra of the

![Raman spectra](image)

**Figure 1.** Raman spectra of pristine shungite powder (1), colloid condensate (2), and aqueous dispersions of shungite carbon nanoparticles with concentration of 0.06 mg/ml (3), and 0.12 mg/ml (4). T = 293°C, laser excitation at 532 nm.
two solids and two aqueous dispersions recorded on a Nicolet Almega XR (Thermo Scientific) spectrometer at laser excitation of 532 nm. The instrument spectral resolution is 1 cm\(^{-1}\) and the laser power is 15 mW. As seen in the figure, practically identical doublets of G and D bands present the main features of the spectra of both solids indicating their close similarity. However, both bands of the condensate are slightly up shifted from 1341 to 1348 cm\(^{-1}\) and from 1586 to 1596 cm\(^{-1}\) for D and G bands, respectively. The data show that the solids are pretty similar, albeit not absolutely identical due to a certain structure rearrangement on the way from pristine shungite to colloid condensation from shungite water dispersions.

In the current graphene science, the relative intensity of the two bands \(I_D/I_G\) is usually considered as a measure of the perfectness of graphene regular structure [12]. However, in relation to such irregular structure as shungite, better to speak differently and to attribute the bands to stretching vibrations of the sp\(^3\) and sp\(^2\) C–C bonds. Evidently, the vibrational frequency of non-distorted benzenoid unit, described by G band, should be close to that of benzene molecule of 1599 cm\(^{-1}\). Once practically inactive in the Raman scattering of the molecule, the vibration is drastically enhanced for the extended set of condensed benzenoid units thus transferring to intense G band that corresponds to the \(\Gamma\)-point \(k = 0\) phonon mode of the graphene crystal. Similarly, D band is characteristic of the distorted benzenoid units on their way to cyclohexanoid ones. The relevant frequencies of stretching vibrations of a set of benzene-to-cyclohexane molecules cover a quite extended interval 1330–1390 cm\(^{-1}\) depending on how many additional hydrogen atoms are added to the benzene ring or how many sp\(^2\) C–C bonds are transformed into sp\(^3\) ones. The position of D bands of both solids fits the interval pretty well indicating that a part of the pristine benzenoid units are distorted toward the cyclohexanoid ones. Similarly to the former, inactive stretching of the pristine cyclohexane is enhanced for the extended set of partial or complete cyclohexanoid units (see the intense \(\Gamma\)-point \(k = 0\) phonon mode at 1342 cm\(^{-1}\) in the experimental Raman spectrum of graphane [13]). Accordingly, the corresponding \(I_D/I_G\) ratio determines the extent of the total sp\(^2\) → sp\(^3\) transformation that is quite similar in the studied solids.

Stretching O–H vibrations of ~3400 cm\(^{-1}\) dominate in the Raman spectra of aqueous dispersions that is why recording of their low-frequency parts presented in Figure 1 required 30-min accumulation. Raman spectra of both dispersions bear the clear imprint of the benzenoid-to-cyclohexanoid transformation presented by D bands located at 1350 cm\(^{-1}\) (curve 3) and 1353 cm\(^{-1}\) (curve 4). It should be noted that the band positions are vividly up shifted with respect to that of the pristine shungite while practically coincide with the position of D band of the colloid condensate. Since the benzenoid-to-cyclohexanoid transformation is quite alike in the two solids, it hardly differs for the dispersion colloids, due to which the shift and relative intensity of their G bands should be similar to that observed for the condensate. Consequently, the relevant G bands of the dispersions, much lower by intensity than D bands, should be located at 1596 ± 4 cm\(^{-1}\) and falls on the low-frequency wing of intense S bands far from their maxima located at 1635 cm\(^{-1}\) (curve 3) and 1627 cm\(^{-1}\) (curve 4). Therefore, the bands should be attributed to Raman scattering from non-carbon scatterer. It is reasonable to suggest the scissor deformational vibrations of water play the role. A shift from the frequency of 1585 cm\(^{-1}\) related to free water molecules to 1627–1635 cm\(^{-1}\) in the dispersions points to the hydrated state of water. The appearance of the vibration, once symmetrically forbidden for free water, with up shifted frequency was observed in the Raman spectra of water retained in clay minerals [14].
The aqueous dispersions exhibit a large number of peculiar properties that, on the one hand, have a direct connection with the unique properties of shungite while on the other hand, are pretty similar to those characteristic for aqueous dispersions of such quantum dots as either Ag and Au nanoparticles or CdS and CdSe nanocompositions, on the one hand, and synthetic graphene quantum dots (see exhausted review [15]), on the other hand. Similarly to the former, shungite quantum dots reveal high activity toward enhancing nonlinear [16–18] and spectral [19] optical properties. Analogously to the latter, shungite dispersions exhibit a close similarity in the appearance of a high inhomogeneity of both morphological and spectral properties. A particular attention should be given to their biomedical behavior [4,20,21]. Thus, the study of the dispersion effect on the behavior of serum albumin showed that shungite globules and proteins form stable bioconjugates. The latter do not change the protein secondary structure, but causes a drastic lowering of the compactness of the protein tertiary structure that might promote various biomedical applications.

3. Shungite in view of graphene molecular chemistry

The graphene-based basic structure of shungite provides a good reason to consider the latter at the microscopic level by using high power of the modern empirical and theoretical molecular science of graphene. This approach allows us not only to explain all the peculiarities of the shungite behavior, but also to lift the veil on the mystery of its origin. To consider shungite from the viewpoint of the graphene molecular science, in fact, is to find answers to the following questions.

(1) Where did graphene-based basic units of shungite come from?
(2) Why is the unit linear size limited to ~1 nm?
(3) What did this size stabilize during the geological time of life?
(4) What is the chemical composition of the basic units?
(5) Why and how do the units aggregate?
(6) Why are there two sets of pores in the shungite carbon?

Knowledge that the molecular graphene science has accumulated for the last years is so vast that it allows considering the totality of issues simultaneously. Obviously, not all the answers to the above questions have been so far fully exhaustive. However, they present the first attempt of seeing the problem as a whole leaving details of the subsequent refinements for future investigations. Currently, the following answers can be suggested.

**Answer 1.** To answer the first question, we have to address the geological story of shungite. Although shungite is about 2 billions years old, its origin has been still under discussion [22]. The available hypothesizes are quite controversial. According to the biogenic concept, it is formed of organic-carbon-rich sediments. Following the others, shungite is of either volcanic endogenous or even extraterrestrial origin. In contrast to graphite, which is largely distributed over the Earth, the shungite deposits are space limited, and the Onega Lake basin of Karelia is the main area for the rock mining.

Two distinct peculiarities are characteristic for the geological Karelian region, namely: (1) shungite deposits around the Onega Lake neighbor with graphites in the vicinity of the Ladoga Lake and (2) there is abundance of water, both open and mineral one, in the former case. The first feature gives clear evidence that the Karelian region as a whole is
favorable for graphene-layer deposition of carbon which might imply the presence of a common framework of the two geological processes. The second forces to draw a particular attention to the aquatic environment of the deposition.

Geology of graphite is well developed by now. According to the modern concept [23], graphite can be (i) either syngenetic, formed through the metamorphic evolution of carbonaceous matter dispersed in the sediments or (ii) epigenetic, originating from precipitation of solid carbon from carbon-saturated C–O–H fluids. Currently, the privilege has been given to the first one. The transformation of carbonaceous matter involves structural and compositional changes of basic structural units in graphite in the form of aromatic lamellae (graphene sheets) and occurs in the nature in the framework of thermal or regional metamorphism that apart from temperature, involves shear strain and strain energy. Temperature from 380°C to ~450°C and pressure between $2 \times 10^8$ Pa (2 kbar) and $3 \times 10^8$ Pa (3 kbar) efficiently govern the graphenization [24,25].

Accepting the syngenetic graphenization (the definition [26] exactly suits the processes occurred) to be a common process for the derivation of both graphite and shungite in the Karelian region, we can suggest the following answer to the first question.

The graphenization is a longtime complicated process that, occurring during a geological scale of time, can be subjected to various chemical reactions. Tempo and character of the reactions are obviously dictated by the environment. It is quite reasonable to suggest that the aqueous environment at 300–400°C, under which the metamorphic evolution of carbonaceous matter occurs, is a dynamically changeable mixture of water molecules, hydrogen and oxygen atoms, hydroxyl and carboxyl radicals as well. The interaction of the carbonaceous matter subjected to structural and compositional changes in the course of alignment of graphene lamellae and pore coalescence with this mixture accompanies the process. The most expected reactions concern hydration, hydrogenation, oxidation, hydroxylation, and carboxylation of the formed lamellae. At this point, it is important to note that, according to the molecular theory of graphene [27–32], any reaction of these kinds primarily involves edge carbon atoms of the sheets. Actually, Figure 2 presents a typical image map of the atomic chemical susceptibility (ACS) distribution over (5, 5) nanographene (NGr) atoms (the latter is presented by a rectangular graphene fragment, below (5, 5) NGr molecule, containing $n_a = 5$ and $n_z = 5$ benzenoid units along armchair and zigzag edges, respectively). The ACS map shape is characteristic for a graphene fragment with bare edge atoms of any size and shape. Presented in Figure 2 shows that the chemical reactivity of the edge atoms exceeds that of the basal plane atoms by approximately four times. Consequently, any addition reaction will start by involving these atoms first. The addition, obviously, terminates the lamellae growth thus limiting the lateral dimensions of the formed graphene layers. Empirically, it has been repeatedly observed in the case of graphene oxide (GO) [33–36]. Therefore, since the above mentioned reactions start simultaneously with the deposit formation, their efficiency determines if either the formed graphene lamellae will increase in size (low efficient reactions) or the lamellae size will be terminated (reactions of high efficiency). Since large graphite deposits are widely distributed over the Earth, it might be accepted that aqueous environment of the organic-carbon-rich sediments generally does not provide suitable conditions for the effective termination of graphene lamellae in the course of the deposit graphitization. Obviously, particular reasons may change the situation that can be achieved in some places of the Earth. Apparently, this occurred in the Onega Lake basin, which caused the replacement of the graphite derivation by the shungite formation. Some geologists
reported on the correlation of shungite formation with the increase of oxygen concentration in atmosphere that took place in 1.9–2.1 Ga [37]. This fits well the geochemical boundary of the Earth history of 2.2 Ga.

**Answer 2.** If chemical modification of graphene lamellae is responsible for limiting their size, the answer to the question about the size limitation to ~1 nm should be sought in the relevant reaction peculiarities. First of all, one must choose among those reactions that are preferable under the pristine graphenization conditions. Including hydroxylation and carboxylation into oxidation reaction, we must make choice among three of them, namely, hydration, hydrogenation, and oxidation. All the three reactions are well studied for graphene at molecular level both empirically and theoretically.

The pristine graphene lamella is hydrophobic so that its interaction with water molecules is weak. Chemical coupling of a water molecule with graphene sheets can rarely occur at the zigzag edge and is characterized by small coupling energy. According to this, water cannot be considered as a serious chemical reactant responsible for the chemical modification of the pristine graphene lamellae. Nevertheless, water plays extremely important role in the shungite fortune that will be discussed later.

Graphene hydrogenation has been actively studied both computationally and experimentally. At molecular level, depending on external conditions concerning the fixation of the sheet perimeter and the accessibility of its basal plane to hydrogen atoms either from
one- or two-sides, different graphene hydrides (GHs) are formed [30]. Empirically (see [38] and references therein), the graphene hydrogenation is a difficult task, and the process usually involves such severe conditions as high temperatures and high pressure or employs special devices, plasma ignition, electron irradiation, and so forth. One of the explanations can be connected with the necessity in overcoming a barrier at each addition of the hydrogen atom to the graphene body. Figure 3 demonstrates the dependence of coupling energies of different addends on their distance from the targeted carbon atom at the zigzag edge of the (5, 5) NGr molecule. In the case of hydrogen, the plotting clearly reveals the barrier that constitutes ~13 kcal/mol.

In contrast, graphene oxidation can apply for a role. The reaction is studied thoroughly at different conditions (see reviews [33–35] and references therein) and the achieved level of its understanding is very high. The latter has led the foundation of massive fabrication of a particular ‘graphene’ that, in fact, is rGO. The oxidation may occur under conditions that provide the shungite derivation in spite of low acidity of the aqueous surrounding but due to long geological time and practically barrierless character of the reaction concerning additions of either oxygen atoms or hydroxyls to the graphene body as seen in Figure 3. As shown, oxidation causes a destruction of both pristine graphite and graphene sheets.
just cutting them into small pieces [34,39]. Thus, 900 s of continuous oxidation cut a large graphene sheet into pieces of ~1 nm in size [34]. Important that further prolongation of the oxidation does not cause decreasing the size thus stabilizing them at the 1 nm level. This finding allows suggesting that shungite sheets of ~1 nm in size have been formed in the course of geologically prolong oxidation of graphene lamellae derived from the graphenization of carbon sediments.

**Answer 3.** Numerous experimental studies (see [34–36, 40–42]) and recent detailed consideration of GOs from the viewpoint of molecular theory [31] showed that the latter are products of the hetero-oxidant reaction. Three oxidants, among which there are oxygen atoms O, hydroxyls OH, and carboxyls COOH, are the main partners of the process albeit in different ways by participating in the formation of the final product. Figure 4 presents final products of the (5, 5) NGr molecule oxidation that follow from the graphene molecular theory. GO molecules I and II were obtained in the course of the stepwise addition of the above oxidants to the molecule under the conditions that the pristine molecule basal plane is accessible for the oxidants either from the top only (Figure 4(a)) or from both sides (Figure 4(b)). The choice of the preferable oxidant was made following the criterion of the largest per step coupling energy [31]. Plottings in

![Figure 4](image-url)

**Figure 4.** Based on the (5, 5) NGr molecule, oxygen-saturated GOs under one-side (top-down exfoliated (5, 5) GO molecule I) (a) and two-side (GO molecule II) (b) oxidation. (c) Per step coupling energy versus step number for the oxides family covering by (5, 5) GO molecules I under subsequent O- and OH-additions to carbon atoms at either the molecule basal plane (curves 1 and 2) or edges (curve 3) [31] (UHF calculations).
Figure 4(c) correspond to the per step coupling energies that describe the energetics of the oxidants attachment in the course of oxidation of GO molecule I (analogous dependences take place for GO molecule II). Contrary to the common opinion, affirmed in the GO science, carboxyl units, located both at the edge of the molecule and at its basal plane, do not meet the criterion and lose a competition to two other oxidants. Once currently investigated, increasing the molecule size allows for revealing a small fraction of the units in the molecule edge area only (see the next subsection below).

Hydrothermal conditions of the shungite derivation present serious arguments in favor of a hypothesis about the GO origin of the deposits. However, the hypothesis strongly contradicts the atomic percentage of oxygen in the carbon-richest shungite rocks that only constitutes a few percents [43] instead of several tens of percents expected from the saturated GOs. This contradiction forces to think about full or partial reduction of the preliminary formed GO occurred during geological process.

As follows from the plottings in Figure 4(c), GO is characterized by two regions of chemical bonding of oxidants with the graphene body. While the edge region should be attributed to that one of strong chemical bonding, the basal plane, for which the average coupling energy is three times less, is evidently related to the area of a weak coupling. The finding is crucial for the GO reduction showing that the latter concerns primarily basal plane while oxidants located in the framing area may not be removed under conditions of the convenient reduction without destruction of the carbon skeleton. This finding explains the residual oxygen content in reduced rGOs of 8–10% [34–36]. As seen, shungite is no exception to this pattern and with low content of oxygen fits the overall picture related to rGOs.

Usually a synthetic GO reduction occurred when using strong reducing agents that are not available in the natural environment of shungite. However, as has been recently shown, the GO reduction can take place just in water, which only requires a much longer time for the process completion [44]. Evidently, the geological time of the shungite derivation is quite enough for the reduction of pristine GOs in water to take place.

Answer 4. Figure 5 presents the equilibrium structures of the (5, 5) rGO and (11, 11) rGO molecules with 1.3 × 1.4 nm² and 10 × 10 nm² cross-section, respectively. The (5, 5) rGO molecule was obtained in the course of the structure optimization after removing all epoxy and hydroxy groups from the basal plane of the (5, 5) GO molecules shown in Figure 4(a) and (b). The (11, 11) rGO molecule was computationally synthesized in the

![Figure 5](image-url)
course of per step oxidation described in detail in Ref. [31]. As seen in Figure 5b, the framing shell of the (11, 11) rGO is replenished with four carboxyl units additionally to carbonyls and hydroxyls as was mentioned earlier.

Due to recovering sp$^2$ configuration for carbon atoms at basal plane, the (5, 5) rGO molecule noticeably regenerates its planarity, although impaired, especially in the corner areas. Basing on empirical estimation of ~1 nm for a basic shungite graphene-based sheet, this molecule, better rGO nanosheet, can be considered as a reliable configuration of the basic shungite structural unit. However, the atomic percentage of oxygen in the case constitutes 24 at% that is far from the empirical contamination. The controversy may mean that the actual oxygen framing of the rGO nanosheets is not fully saturated. A large oscillation amplitude of the per step coupling energy related to the framing area (see curve 3 in Figure 4(c)) may be one of possible reasons. Actually, the atoms, which correspond to the top part of the plotting, may be removed during the reduction additinally to the basal ones. Another reason can be connected with the stability of the rGO sheets that depends on the sheet shape and corner structure, on the one hand, and thermodynamic conditions of the oxygen reservoir, on the other hand [45]. At any rates, the problem needs a further examination.

Answer 5. Assuming that rGO nanosheets generated in aqueous media present the first stage of shungite derivation, let us trace their path from individual molecules to densely packed shungite carbon. Obviously, the path is through successive stages of the sheets aggregation. Empirically was proven that aggregation is characteristic for synthetic GO and rGO sheets as well. Thus, infrared absorption [46] and inelastic incoherent neutron scattering (IINS) [47,48] showed that synthetic GO forms stacked turbostratic structures that confine water. Just recently, a similar picture was obtained for synthetic rGO [49] and shungite [10,49]. Neutron diffraction showed therewith [10,48,49] that the characteristic graphite interfacial distance $d_{002}$ constitutes, in average, ~6.9 Å in the case of GO and reduces to ~3.5 Å for rGO of both synthetic and natural origin, evidently indicating the recovery of the GO carbon carcass planarity due to its reduction. Computationally, it was confirmed [48] that water molecules are comfortably located between the neighboring layers of the GO stacked structure while none of the water molecules can be retained near the rGO basal plane (see Figure 6). Regardless of the molecule starting position, each of them is displayed outside the rGO basal plane area once kept in the vicinity of framing atoms. The finding is well correlated with the rGO short-packed stacked structure leaving the place for water molecules confinement in pores formed by the stacks. The IINS study [10] has proven the pore location of retained water in shungite and confirms that the rGO nanosheets present the basic structural units of shungite thus allowing for suggesting a vision of the next stages of the shungite structure toward shungite rocks.

The characteristic $d_{002}$ diffraction peaks of shungite are considerably broadened in comparison with those of graphite, which allows for estimating approximate thickness of the stacks of ~1.5 nm [10] that corresponds to five- and six-layered rGO sheets. The stacks form the secondary structure of shungite. Aggregating, the stacks are combined in globules, a planar view of one of possible models of which is presented in Figure 7. The globules of a few nanometer in size present the third stage of the shungite fractal structure [1]. The inner surface of the pores is mainly carpeted with oxygen atoms that can willingly hold water molecules in their vicinity as follows from Figure 6. Thus retained water is the main content of the registered IINS spectra [10]. Further aggregation of the
globules leads to the formation of bigger aggregates with lateral dimensions of 20–100 nm. The aggregate agglomeration completes the formation of the fractal structure of shungite.

**Answer 6.** In fractal structures, which are rich in pores, the pore size is usually tightly connected with the lateral dimension of structural elements involved in the pore formation [50]. Moreover, the larger is variety of the elements size and structure, the bigger is distribution of the pores over size. In view of this, the different size of the multilevel shungite fractal structural elements evidently predetermines different sizes of shungite pores. Thus, as seen in Figure 7, the irregular distribution of stacks in space causes the formation of different interglobular pores, linear dimensions of which are comparable with those of stacks. Actually, one of the linear sizes of the pores formed by rGO nanosheets is determined by linear dimensions of the latter while two others are defined by the thickness of the sheet stacks. Therefore, basic rGO nanosheets and their stacks are responsible for shungite pores of 2–5 nm in size. Following this line, globules may form pores up to 10 nm while extended aggregates of globules obviously form pores of a few tens nanometer and bigger. This presentation well correlates with the SANS experimental data that evidence the presence of two sets of pores in shungite in the range of 2–10 nm and above 100 nm [6]. Taking together, the multitier of structural elements and various porosity make the fractal structure of shungite good self-consistent.

4. **Conclusive remarks**

The main idea discussed in the current article is that molecular chemistry at the grafhenization stage lays the foundation of the difference in graphite and shungite derivation under natural conditions during the geological time. The concept showed the way of checking this suggestion by exhibiting chemical reactions that are responsible for the deposits derivation as well as by simulating final products of the relevant reactions. Based
on the theory of graphite genesis [23], the reaction participants involve molecular objects simulating fragments of polycondensed benzenoid molecules (carbon substrate, or naked graphene lamellae), on the one hand, and molecular (water, carboxyl, hydroxyl) as well as atomic (hydrogen, oxygen) species (chemical reactants), on the other hand. As follows from the molecular theory of graphene [32] and general grounds of the chemistry for nanoscience [51], the naked graphene lamellae are kinetically unstable since covalent bonds are cut at their edges. Such species will try to heal themselves and external molecules may stabilize them. In full agreement with our suggestion, Hoffmann continues [51] that ‘too great stabilization will inhibit growth; too little stabilization will not prevent from collapse to the solid’. The difference in the graphene lamellae stabilization was the second basic idea of our approach. Thus, the great stabilization of the lamellae results in
the shungite formation while the little one provides derivation of graphite deposits. The stabilizing reactions are controlled by the reactants coming on and off the pristine naked graphene lamellae while both thermodynamic (Gibbs energies) and kinetic (activation energies) factors matter in the dynamic process. Shungite is suggested to be formed as a result of a balance of a number of multi-reactant processes, each governed by its own thermodynamics and kinetics. The presence of other elements such as silicon and metals undoubtedly influences the deposit formation. Actually, the Karelian deposits of shungite are non-uniform by the carbon content, value of which changes from 3% to 98 wt% [1]. Silica is the main partner of the mixed depositions. However, speaking about shungite as carbon allotrope, we imply a particular shungite rock from the Shun’ga deposit with the highest carbon content up to 98.8% [43] for which the presence of other Earth element is negligible [52].

The two main concepts have been considered in the article addressing oxidation/reduction reactions that govern chemical modification of the pristine graphene lamellae. Basing on a wide experience gained for graphene chemistry in the laboratory conditions and an extended computational system experiment performed earlier [31], the oxidation/reduction reactions are shown to have a big privilege against hydration and hydrogenation of graphene. The two reactions work simultaneously but serving different purposes: oxidation stabilizes the growth of pristine graphene lamellae thus determining their size, while reduction releases the oxygenated nanosheets from weakly bound reactants located through over basal plane and partially at the sheets perimeter leaving remaining in the sheet circumference thus preserving their stabilization. This conclusion is in full agreement with shungite empirical data related to exhibiting (1) ~1 nm planar-like sheets of rGO as the basic structural element of the macroscopic shungite structure and (2) remaining low content of oxygen in the most carbon-pure shungite samples.

Shungite is formed in aqueous surrounding and although water molecules do not act as active chemical reactants at the oxidation stage, they play a very important role at the reduction [44] as well as in composing shungite as a solid. First, the slow rate of reduction evidently favors the accumulation of rGO nanosheets during a long shungite geological story. Should not to exclude also a possible chemical modification of the sheets framing due to their long stay in hot water. Second, water molecules fill the pores, helping to strengthen the framework of fractal shungite carbon. These processes, when taken together, have led to the creation of a unique natural pantry of nanoscale rGO.

Acknowledgments
The work was supported by Basic Research Program, RAS, Earth Sciences Section-5 and grant RFBI 13-03-00422. The authors are grateful to N. Popova for assisting in the barrier calculations.

References
[1] N.N. Rozhkova, Shungite Nanocarbon (in Russian), Karelian Research Centre of RAS, Petrozavodsk, 2011.
[2] N.N. Rozhkova, A.V. Gribanov, and M.A. Khodorkovskii, Water mediated modification of structure and physical chemical properties of nanocarbons, Diamond Relat. Mater. 16 (2007), pp. 2104–2108.
[3] N.N. Rozhkova, G.I. Emel’yanova, L.E. Gorlenko, A. Jankowska, M.V. Korobov, and V.V. Lunin, Structural and physico-chemical characteristics of shungite nanocarbon as revealed through modification, Smart Nanocomposites 1 (2010), pp. 71–90.
14

E.F. Sheka and N.N. Rozhkova

[4] S.P. Rozhkov, N.N. Rozhkova, G.A. Suhanova, A.G. Borisova, and A.G. Goryunov, DSC data on interaction of carbon nanoparticles with protein molecules, in Nanoparticles in Condensed Media, P.A. Vityaz, ed., Publishing Center BSU, Minsk, 2008, pp. 134–139.

[5] N.N. Rozhkova, L.E. Gorlenko, G.I. Emel'yanova, M.V. Korobov, V.V. Lunin, and E. Osawa, The effect of ozone on the structure and physico-chemical properties of ultradisperse diamond and shungite nanocarbon elements, Pure Appl. Chem. 81 (2009), pp. 2093–2105.

[6] M.V. Avdeev, T.V. Tropin, V.L. Akseenov, L. Rosta, V.M. Garamus, and N.N. Rozhkova, Pore structures in shungites as revealed by small-angle neutron scattering, Carbon 44 (2006), pp. 954–961.

[7] V.V. Koval’evski, N.N. Rozhkova, A. Zaidenberg, and A.N. Yermolin, Fullerene-like structures in shungite and their physical properties, Mol. Mat. 4 (1994), pp. 77–80.

[8] N.N. Rozhkova, G.I. Emel’yanova, L.E Gorlenko, A.V. Gribanov, and V.V. Lunin, From stable aqueous dispersion of carbon nanoparticles to the clusters of metastable carbon of shungites, Glass Phys. Chem. 37 (2011), pp. 621–626.

[9] N.N. Rozhkova, Aggregation and stabilization of shungite carbon nanoparticles, Ecol. Chem. 4 (2012), pp. 240–251.

[10] E.F. Sheka, N.N. Rozhkova, I. Natkaniec, and K. Holderna-Natkaniec, Inelastic neutron scattering study of reduced graphene oxide of natural origin, JETP Lett. 99 (2014).

[11] F.K. Smidt, Fractals in Physical Chemistry of Heterogeneous Systems and Processes (in Russian), Irkutsk University, Irkutsk, 2000.

[12] M.A. Pimental, G. Dresselhaus, M.S. Dresselhaus, L.A. Cancado, A. Jorio, and R. Sato, Studying disorder in graphite-based systems by Raman spectroscopy, Phys. Chem. Chem. Phys. 9 (2007), pp. 1276–1290.

[13] D.C. Elias, R.R. Nair, T.M.G. Mohiuddin, S.V. Morozov, P. Blake, M.P. Halsall, A.C. Ferrari, D.W. Boukhvalov, M.I. Katsnelson, A.K. Geim, and K.S. Novoselov, Control of graphene’s properties by reversible hydrogenation: Evidence for graphene, Science 323 (2009), pp. 610–613.

[14] A.B.H. Amara, X-ray diffraction, infrared and TGA/DTG analysis of hydrated nacrite, Clay Minerals 32 (1997), pp. 463–470.

[15] L. Li, G. Wu, G. Yang, J. Peng, J. Zhao, and J.-J. Zhu, Focusing on luminescent graphene quantum dots: current status and future perspectives, Nanoscale 5 (2013), pp. 4015–4039.

[16] I.M. Belousova, I.M. Kislyakov, D.A. Videnichev, N.N. Rozhkova, and A.G. Tupolev, Shungite carbon as a material for optical limiting of high intensity laser radiation in the visible and near infrared region. Abstracts, 9th Biennal Int Workshop on Fullerenes and Atomic Clusters, (St. Petersburg, Russia) Ioffe Phys-Techn Inst. RAS. (2009), p. 222.

[17] N.V. Kamanina, S.V. Serov, N.A. Sharpo, and N.N. Rozhkova, Photoinduced changes in refractive index of nanostructured shungite-containing polyimide systems, Tech. Phys. Lett. 37 (2011), pp. 949–951.

[18] N.V. Kamanina, S.V. Serov, N.A. Sharpo, S.V. Likhomanova, D.N. Timonin, P.V. Kuzhakov, N.N. Rozhkova, I.V. Kityk, K.J. Plucinski, and D.P. Uskokovic, Polyimide-fullerene nanostructured materials for nonlinear optics and solar energy applications, J. Mater. Sci.: Mater. Electron 23 (2012), pp. 1538–1542.

[19] B.S. Razbirin, N.N. Rozhkova, E.F. Sheka, D.K. Nelson, A.N. Starukhin, and A.S. Goryunov. Fractals of graphene quantum dots in photoluminescence of shungite. arXiv:1308.2569v2 [cond-mat.mes-hall] 2013.

[20] A.S. Goryunov, A.G. Borisova, and S.P. Rozhkov. Raman spectroscopy of bioconjugates of bovine serum albumin and shungite nanocarbon. Proc. Karelian Res. Center RAS, Exp. Biol. Ser. 2 (2012), pp. 154–158.

[21] S. Rozhkov, G. Sukhanova, A. Borisova, N. Rozhkova, and A. Goryunov, Effects of carbon nanoparticles on protein thermostability revealed by DSC and ESR spin-labelling methods, Ann. World Conf. Carbon Biarritz (France) (2009), p. 201.

[22] V.A. Melezhik,  A.E. Fallick,  M.M. Filipov,  A. Lepland,  D.V. Rychanchik,  Y.E. Deines,  P.V. Medvedev,  A.E. Romashkin,  and H. Strauss, Petroleum surface oil seeps from a Paleoproterozoic petrified giant oilfield, Terra Nova. 21 (2009), pp. 119–126.

[23] B. Kwiecińska and H.I. Petersen, Graphite, semi-graphite, natural coke, and natural char classification – ICCP system, Int. J. Coal. Geol. 57 (2004), pp. 99–116.
[24] C.A. Landis, *Graphitization of dispersed carbonaceous material in metamorphic rocks*, Contrib. Mineral Petrol. 30 (1971), pp. 34–45.

[25] C.F.K. Diessel and R. Offler, *Change in physical properties of coalified and graphitized phytoelects with grade of metamorphism*, Neues. Jahrb. Mineral Monatsh H. 1 (1975), pp. 11–26.

[26] A. Bianco, H.-M. Cheng, T. Enoki, G. Yu, R.H. Hurt, and N. Koratkar, *All in the graphene family – a recommended nomenclature for two-dimensional carbon materials*, Carbon 65 (2013), pp. 1–6.

[27] E.F. Sheka and L.A. Chernozatskii, *Chemical reactivity and magnetism of graphene*, Int. J. Quant. Chem. 110 (2010), pp. 1938–1946.

[28] E.F. Sheka and L.A. Chernozatskii, *Broken spin symmetry approach to chemical susceptibility and magnetism of graphenium species*, J. Exp. Theor. Phys. 110 (2010), pp. 121–132.

[29] E.F. Sheka, *Fullerenes: Nanochemistry, Nanomagnetism, Nanomedicine, Nanophotonics*, CRC Press, Taylor and Francis Group, Boca Raton, FL, 2011.

[30] E.F. Sheka and N.A. Popova, *Odd-electron molecular theory of the graphene hydrogenation*, J. Mol. Mod. 18 (2012), pp. 3751–3768.

[31] E.F. Sheka and N.A. Popova, *Molecular theory of graphene oxide*, Phys. Chem. Chem. Phys. 15 (2013), pp. 13304–13322.

[32] E.F. Sheka, *Computational strategy for graphene: Insight from odd electrons correlation*, Int. J. Quant. Chem. 112 (2012), pp. 3076–3090.

[33] D.R. Dreyer, S. Park, C.W. Bielawski, and R.S. Ruoff, *The chemistry of graphene oxide*, Chem. Soc. Rev. 39 (2010), pp. 228–240.

[34] W. Hui and H.H. Yun, *Effect of oxygen content on structures of graphite oxides*, Ind. Eng. Chem. Res. 50 (2011), pp. 6132–6137.

[35] T. Kuila, S. Bose, A.K. Mishra, P. Khanra, N.H. Kim, and J.H. Lee, *Chemical functionalization of graphene and its applications*, Prog. Mat. Sci. 57 (2012), pp. 1061–1105.

[36] A.M. Dimiev, L.B. Alemany, and J.M. Tour, *Graphene oxide. Origin of acidity, its instability in water, and a new dynamic structural model*, ACS Nano. 7 (2013), pp. 576–584.

[37] A.I. Golubev, A.E. Romashkin, and D.V. Rychanchik, *Relation of carbon accumulation to Paleoproterozoic basic volcanism in Karelia (Jatulian-Ludicovian transition)*, Geol. Useful Minerals Karelia 13 (2010), pp. 73–79.

[38] W. Chen, Z. Zhu, S. Li, C. Chen, and L. Yan, *Efficient preparation of highly hydrogenated graphene and its application as a high-performance anode material for lithium ion batteries*, Nanoscale 4 (2012), pp. 2124–2129.

[39] S. Pan and I.A. Aksay, *Factors controlling the size of graphene oxide sheets produced via the graphite oxide route*, ACS Nano 5 (2011), pp. 4073–4083.

[40] V. Singh, D. Joung, L. Zhai, S. Das, S.I. Khondaker, and S. Seal, *Graphene based materials: Past, present and future*, Prog. Mat. Sci. 56 (2011), pp. 1178–1271.

[41] A.L. Ivanovskii, *Graphene-based and graphene-like materials*, Russ. Chem. Rev. 81 (2012), pp. 571–605.

[42] Y.Z. By, M. Shanthi, C. Weiwei, L. Xuesong, W.S. Ji, J.R. Potts, and R.S. Ruoff, *Graphene and graphene oxide: Synthesis, properties, and applications*, Adv. Mater. 22 (2010), pp. 3906–3924.

[43] M.M. Filippov, *Shungitonosnyje porody Onezhskoj struktury (Shungite Rocks of Onega’s Structure)* (Russian), Karelian Research Centre of RAS, Petrozavodsk, 2002.

[44] K.-H. Liao, A. Mittal, S. Bose, C. Leighton, K.A. Mkhoyan, and C.W. Macosko, *Aquoeous only route toward graphene from graphite oxide*, ACS Nano. 5 (2011), pp. 1253–1258.

[45] H. Shi, L. Lai, I.K. Snook, and A.S. Barnard, *Relative stability of graphene nanosheets under environmentally relevant conditions*, J. Phys. Chem. C. 117 (2013), pp. 15375–15382.

[46] M. Acić, C. Mattevi, C. Gong, G. Lee, K. Cho, M. Chhowalla, and Y.J. Chabal, *The role of intercalated water in multilayered graphene oxide*, ACS Nano. 4 (2010), pp. 5861–5868.

[47] A. Buchsteiner, A. Lerf, and J. Pieper, *Water dynamics in graphite oxide investigated with neutron scattering*, J. Phys. Chem. B. 110 (2006), pp. 22328–22338.

[48] I. Natkaniec, K. Druzbiicki, S.P. Gubin, K. Holdema-Natkaniec, S.V. Tkachev, and E.F. Sheka, *IINS and DFT studies of vibrational spectra of water retained in graphene oxide*. 2nd satellite
workshop of ICNS 2013 on Dynamics of Molecules and Materials, University of Glasgow, Glasgow, Scotland, 2013, p. 21.

[49] E.F. Sheka, N.N. Rozhkova, I. Natkaniec, K. Holdema-Natkaniec, and K. Druzbicki, Water dynamics in shungite with inelastic neutron scattering, International Conference on Advanced Carbon Nanostructure, Ioffe Phys-Techn Inst RAS, St. Petersburg, Russia, 2013, p. 68.

[50] J.-F. Gouyet, Physics and Fractal Structures, Masson Springer, Paris/New York, 1996.

[51] R. Hoffmann, Small but strong lessons from chemistry for nanoscience, Ang. Chem. Int. Ed. 52 (2013), pp. 93–103.

[52] N.N. Rozhkova, A.Z. Zaidenberg, and A.I. Golubev. Challenges to chemical geology. Refereed papers from MAEGS-10. Prague. Czech Geological Survey 1998; MAEGS-10. Prague, pp. 137–143.