

# Research of Influence of Shungite on Mountain Water from Bulgaria. Mathematical Models of Water Influenced from Shungite and Zeolite

Ignat Ignatov<sup>1\*</sup> Oleg Mosin<sup>2</sup>

1. Scientific Research Center of Medical Biophysics (SRCMB),

N. Kopernik Street, 32, Sofia 1111, Bulgaria

2. Biotechnology Department, Moscow State University of Applied Biotechnology,

Talalikhina Street, 33, Moscow 109316, Russian Federation

\* E-mail of the corresponding author: [mbioph@dir.bg](mailto:mbioph@dir.bg)

## Abstract

We studied the composition and structural properties of amorphous, uncrystallized, fullerene analogous carbon containing natural mineral shungite from Zazhoginskoe deposit in Karelia (Russian Federation) and microporous crystalline aluminosilicate mineral zeolite (Most, Bulgaria). There are submitted data about the nanostructure, obtained with using of transmission electron microscopy (TEM-method), IR-spectroscopy (NES and DNES-method), as well as composition and physical chemical properties of these minerals. The average energy ( $\Delta E_{H...O}$ ) of hydrogen H...O-bonds among individual molecules H<sub>2</sub>O after treatment of shungite and zeolite with water is measured at -0.1137 eV for shungite and -0.1174 eV for zeolite. The calculation of  $\Delta E_{H...O}$  for shungite with using DNES method compiles  $0.0025 \pm 0.0011$  eV and for zeolite  $-1.2 \pm 0.0011$  eV. This result suggests the restructuring of  $\Delta E_{H...O}$  values among H<sub>2</sub>O molecules with a statistically reliable increase of local maximums in DNES-spectra. Also are demonstrated the prospects of using shungite, possessing high absorption, catalytic and bactericidal activity, as an adsorbent in water-treatment, water purification, and other industries.

**Keywords:** shungite, zeolite, nanostructure, fullerenes, water treatment, water purification

## 1. Introduction

Shungite and zeolite – the minerals refer to new generation of natural mineral sorbents (NMS). Shungite is an intermediate form between the amorphous carbon and the graphite crystal containing carbon (30%), silica (45%), and silicate mica (about 20%) (Khavari-Khorasani & Murchison, 1979). Shungite carbon is a fossilized organic material of sea bottom Precambrian sediments of high level of carbonization containing the fullerene-like regular structures. Shungite got its name after the village of Shunga in Karelia (Russian Federation), located on the shore of Onezhskoe Lake, where is located the only one mineral Zazhoginsky deposit of shungites on the territory of the Russian Federation. The total shungite reserves of Zazhoginsky deposit amount to approximately 35 million tons of shungite. The plant production capacity for the mining and processing of shungite makes up 200 thousand tons of shungite per year.

Zeolites are the aluminosilicate members of the family of microporous solids known as "molecular sieves",

named by their ability to selectively sort molecules based primarily on a size exclusion process. Natural zeolites form when volcanic rocks and ash layers react with alkaline groundwater. Zeolites also crystallize in post-depositional environments over periods ranging from thousands to millions of years in shallow marine basins. Naturally occurring zeolites are rarely pure and are contaminated to varying degrees by other minerals, metals, quarts, or other zeolites. For this reason, naturally occurring zeolites are excluded from many important commercial applications where uniformity and purity are essential.

As natural minerals shungite and zeolite has unusually broad scope of application in industry. Shungite was used initially, mainly as a filler and substitute of the carbon coal coke (fuel) in blast furnace production of high-silicon cast iron, in ferroalloys melting, in the production of non-stick heat-resistant paints and coatings, and as a filler in rubber production. Subsequently there were discovered other new valuable properties of shungite – adsorptional, bactericidal, catalytic, reduction-oxidation properties, as well as the ability of shungite minerals to screen off electromagnetic and radio radiations. These properties have made the use of shungite in various branches of science, industry and technology, for creating on its basis a variety of new nanotechnological materials with nano-molecular structure. On the basis of shungite have been created new conductive paints, fillers for plastic materials, rubber and carbon black substitutes, composite materials, concrete, bricks, stuccoing plasters, asphalts, as well as materials having bactericidal activity, and materials shielding off the radio and electromagnetic radiation. Adsorptional, catalytic, and reduction-oxidation properties of shungite favored its use in water treatment and water purification technologies, i.g. in treatment of sewage waters from many organic and inorganic substances (heavy metals, ammonia, organochlorine compounds, petroleum products, pesticides, phenols, surfactants, etc.). Moreover, shungite has a strongly marked biological activity and bactericidal properties.

Zeolites as shungites are widely used in industry as a desiccant of gases and liquids, for treatment of drinking and sewage water from heavy metals, ammonia, phosphorus, as catalyst in petrochemical industry for benzene extraction, for production of detergents and for extracting of radionuclides in nuclear reprocessing. They are also used in medicine as nutritional supplements having antioxidant properties.

A wide range of properties of shungite and zeolite defines the search for new areas of industrial application of these minerals in science and technology that contributes to a deeper study of the structure with using the modern analytical methods. This paper deals with investigation of the structural properties of shungite and zeolite and their composition.

## **2. Materials and Methods**

### ***2.1. Materials***

The study was performed with samples of shungite obtained from Zazhoginsky deposit (Karelia, Russia) and zeolite (Most, Bulgaria). Samples were taken *and* analyzed in solid samples according to National standard of the Russian Federal Agency of Technical Regulation and Metrology. Samples were put into 100 cm<sup>3</sup> hermetically sealed glass tubes after being washed in dist. H<sub>2</sub>O and dried in crucible furnace, and homogenized in homogenizer by mechanical grinding. For the decomposition of the shungite samples a system of microwave decomposition was used. Other methods of samples processing were washing with

dist. H<sub>2</sub>O, drying, and homogenization on cross beater mill Retch SK100 (“Retsch Co.”, Germany) and Pulverisette 16 (“Fritsch GMBH”, Germany).

## **2.2. Analytical Methods**

The analytical methods were accredited by the Institute of Geology of Ore Deposits. Petrography, Mineralogy, and Geochemistry (Russian Academy of Sciences). Samples were treated by various methods as ICP-OES, GC, and SEM.

## **2.3. Gas-Chromatography**

Gas-chromatography (GC) was performed at Main Testing Centre of Drinking Water (Moscow, the Russian Federation) on Kristall 4000 LUX M using Chromaton AW-DMCS and Inerton-DMCS columns (stationary phases 5% SE-30 and 5% OV-17), equipped with flame ionization detector (FID) and using helium (He) as a carrier gas.

## **2.4. Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES)**

The mineral composition of shungite was studied by inductively coupled plasma optical emission spectrometry (ICP-OES) on Agilent ICP 710-OES (Agilent Technologies, USA) spectrometer, equipped with plasma atomizer (under argon stream), MegaPixel CCD detector, and 40 MHz free-running, air-cooled RF generator, and Computer-optimized echelle system: the spectral range at 167–785 nm; plasma gas: 0–22.5 l/min in 1.5 l/min; power output: 700–1500 W in 50 W increments.

## **2.5. Elemental Analysis**

The total amount of carbon (C<sub>total</sub>) in shungite was measured according to the ISO 29541 standard using elemental analyzer CHS-580 (“Eltra GmbH”, Germany), equipped with electric furnace and IR-detector by combustion of 200 mg of solid homogenized sample in a stream of oxygen at the temperature 1500 °C.

## **2.6. Transmission Electron Microscopy (TEM)**

The structural studies were carried out with using JSM 35 CF (JEOL Ltd., Korea) device, equipped with X-ray microanalyzer “Tracor Northern TN”, SE detector, thermomolecular pump, and tungsten electron gun (Harpin type W filament, DC heating); working pressure: 10<sup>-4</sup> Pa (10<sup>-6</sup> Torr); magnification: 300.000, resolution: 3.0 nm, accelerating voltage: 1–30 kV; sample size: 60–130 mm.

## **2.7. IR-Spectroscopy**

IR-spectra of water samples, obtained after being contacted 3 days with shungite and zeolite, were registered on Fourier-IR spectrometer Bruker Vertex (“Bruker”, Germany) (a spectral range: average IR – 370–7800 cm<sup>-1</sup>; visible – 2500–8000 cm<sup>-1</sup>; the permission – 0.5 cm<sup>-1</sup>; accuracy of wave number – 0.1 cm<sup>-1</sup> on 2000 cm<sup>-1</sup>); Non-equilibrium Spectrum (NES) and Differential Non-equilibrium Spectrum (DNES).

## **3. Results and Discussions**

### 3.1. Structure of shungite

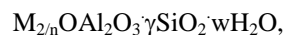
According to the last structural studies shungite is a metastable allotropic form of carbon with high level of carbonization (carbon metamorphism), being on prior to graphite stage of coalification (Volkova & Bogdanov, 1986). Along with carbon the shungite, obtained from Zazhoginsky deposit in Karelia (Russian Federation) contains SiO<sub>2</sub> (57.0%), TiO<sub>2</sub> (0.2%), Al<sub>2</sub>O<sub>3</sub> (4.0%), FeO (0.6%), Fe<sub>2</sub>O<sub>3</sub> (1.49%), MgO (1.2%), MnO (0.15%), K<sub>2</sub>O (1.5%), S (1.2%) (Table 1). The product obtained after the thermal firing of shungite (shungizit) at 1200–1400 °C contains in small amounts V (0.015%), B (0.004%), Ni (0.0085%), Mo (0.0031%), Cu (0.0037%), Zn (0.0067%), Co (0.00014%) As (0.00035%), Cr (0.72%), Zn (0.0076%) and other elements (Table 2).

In comparison with shungite zeolite comprises a microporous crystalline aluminosilicate mineral commonly used as commercial adsorbents, three-dimensional framework of which is formed by linking via the vertices the tetrahedra [AlO<sub>4</sub>]<sup>2-</sup> and [SiO<sub>4</sub>]<sup>2-</sup> (Panayotova & Velikov, 2002). Each tetrahedron [AlO<sub>4</sub>]<sup>2-</sup> creates a negative charge of the carcasses compensated by cations (H<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, NH<sub>4</sub><sup>+</sup>, etc.), in most cases, capable of cation exchange in solutions. Tetrahedrons formed the secondary structural units, such as six-membered rings, five-membered rings, truncated octahedra, etc. Zeolite framework comprises interacting channels and cavities forming a porous structure with a pore size of 0.3–1.0 nm. Average crystal size of the zeolite may range from 0.5 to 30 μm.

Table 1. The chemical composition of shungites from Zazhoginsky deposit (Karelia, Russian Federation), in % (w/w)

№	Chemical component	Content, % (w/w)
1	C	30.0
2	SiO <sub>2</sub>	57.0
3	TiO <sub>2</sub>	0.2
4	Al <sub>2</sub> O <sub>3</sub>	4,0
5	FeO	0.6
6	Fe <sub>2</sub> O <sub>3</sub>	1.49
7	MgO	1.2
8	MnO	0.15
9	CaO	0.3
10	Na <sub>2</sub> O	0.2
11	K <sub>2</sub> O	1.5
12	S	1.2
13	H <sub>2</sub> O	1.7

The empirical formula of zeolite can be represented as:



where n – the cationic charge (n = 1–2), γ – the molar ratio of oxides of silicon and aluminum in the zeolite framework, indicating the amount of cation exchange positions in the structure (y = 2–∞), w – the amount

of water.

Table 2. The chemical composition of shungite after heat treatment at 1200–400 °C

№	Chemical component	Content, % (w/w)
1	C	26.25
2	SiO <sub>2</sub>	3.45
3	TiO <sub>2</sub>	0.24
4	Al <sub>2</sub> O <sub>3</sub>	3.05
5	FeO	0.32
6	Fe <sub>2</sub> O <sub>3</sub>	1.01
7	MgO	0.56
8	MnO	0.12
9	CaO	0.12
10	Na <sub>2</sub> O	0.36
11	K <sub>2</sub> O	1.23
12	S	0.37
14	P <sub>2</sub> O <sub>3</sub>	0.03
15	Ba	0.32
16	B	0.004
17	V	0.015
18	Co	0.00014
19	Cu	0.0037
20	Mo	0.0031
21	As	0.00035
22	Ni	0.0085
23	Pb	0.0225
24	Sr	0.001
26	Cr	0.0072
26	Zn	0.0067
27	H <sub>2</sub> O	0.78
28	Calcination (burning) losses	32.78

The composition of zeolite is analogous to that of shungite (Table 3), except for carbon which does not occur in zeolite. The amounts of core elements (SiO<sub>2</sub>, TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, FeO, Fe<sub>2</sub>O<sub>3</sub>, MgO, CaO, Na<sub>2</sub>O, K<sub>2</sub>O, S) constituting these minerals differ from that of shungite: their content is higher than that of shungite except for TiO<sub>2</sub> and K<sub>2</sub>O, the contents of which in zeolite were decreased (Table 3). The content of microelements as V (0.0272%), Co (0.0045%), Cu (0.0151%), Mo (0.0012%), As (0.0025%), Ni (0.0079%), Zn (0.1007%), Zn (0.1007%) was somewhat increased in zeolite, while the content of Ba (0.0066%) and Cr (0.0048%)

was increased (Table 3).

Table 3. The chemical composition of zeolite (Bulgaria), in % (w/w)

№	Chemical component	Content, % (w/w)
1	SiO <sub>2</sub>	22.14
2	TiO <sub>2</sub>	0.01
3	Al <sub>2</sub> O <sub>3</sub>	17.98
4	FeO	23.72
5	Fe <sub>2</sub> O <sub>3</sub>	1.49
6	MgO	14.38
7	MnO	0.61
8	CaO	0.36
9	Na <sub>2</sub> O	0.5
10	K <sub>2</sub> O	0.4
11	S	0.32
12	P <sub>2</sub> O <sub>5</sub>	0.06
13	Ba	0.0066
14	V	0.0272
15	Co	0.0045
17	Cu	0.0151
18	Mo	0.0012
19	As	0.0025
20	Ni	0.0079
21	Pb	0.0249
22	Sr	0.0021
23	Cr	0.0048
24	Zn	0.1007
25	H <sub>2</sub> O	1.43

Physical and chemical properties of shungite have been sufficiently studied (Parfen'eva, 1994). Density of shungite 2.1–2.4 g/cm<sup>3</sup>; porosity – up to 5%; the compressive strength – 1000–1200 kgf/cm<sup>2</sup>; conductivity coefficient – 1500 SI/m; thermal conductivity coefficient – 3.8 W/mK, the adsorption capacity up to 20 m<sup>2</sup>/g.

Shungites differ in composition of mineral matrix (aluminosilicate, siliceous, carbonate), and the amount of carbon in shungite samples. Shungite minerals with silicate mineral basis are divided into low-carbon (5% C), medium-carbon (5–25% C), and high-carbon shungites (25–80% C) (Kasatochkin et al., 1978). The sum (C + Si) in shungites of Zazhoginsky deposit (Karelia, Russian Federation) is varied within 83–88% as shown in Figure 1.

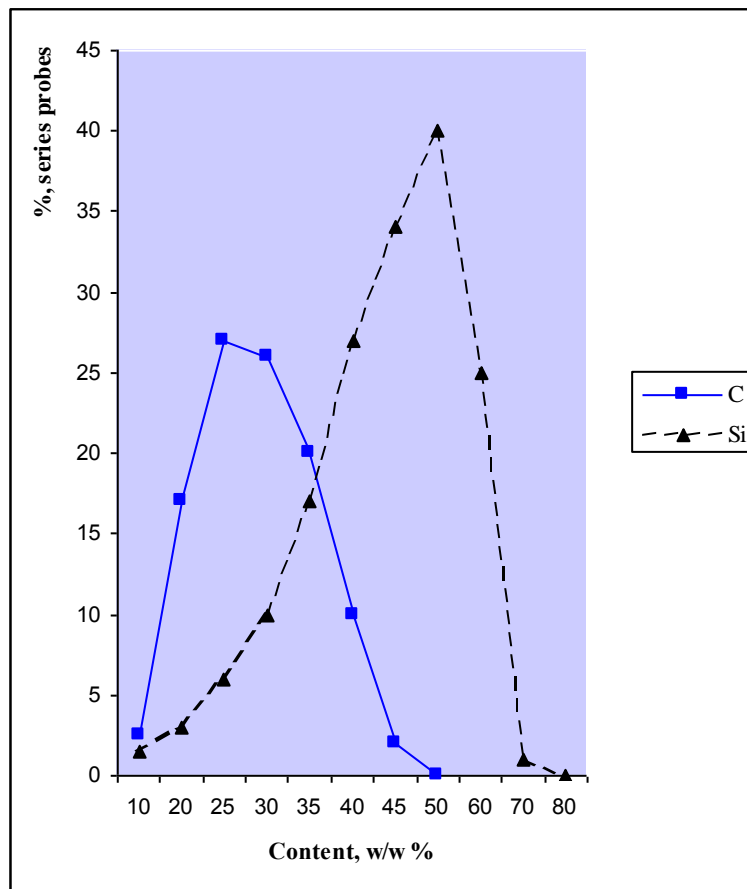


Figure 1. The distribution (%) of carbon (C) (solid line) and silicon (Si) (dotted line) in shungite samples from Zazhoginsky deposit (Karelia, Russian Federation) according to atomic emission spectrometry (AES)

The crystals of crushed, fine ground shungite possess strong bipolar properties. This results in a high adhesion, and the ability of shungite to mix with almost all organic and inorganic substances. Besides, shungite has a broad spectrum of bactericidal properties; the mineral is adsorptive active against some bacterial cells, phages, and pathogenic saprophytes (Khadartsev & Tuktamyshev, 2002).

The unique properties of the mineral are defined by nanostructure and composition of its constituent elements. Shungite carbon is equally distributed in the silicate framework of fine dispersed quartz crystals having the size of 1–10  $\mu\text{m}$  (Kovalevski, 1994; Mosin & Ignatov, 2013a), as confirmed by studying of ultra-thin sections of shungite by transmission electron microscopy (TEM) in absorbed and backscattered electrons (Figure 2).

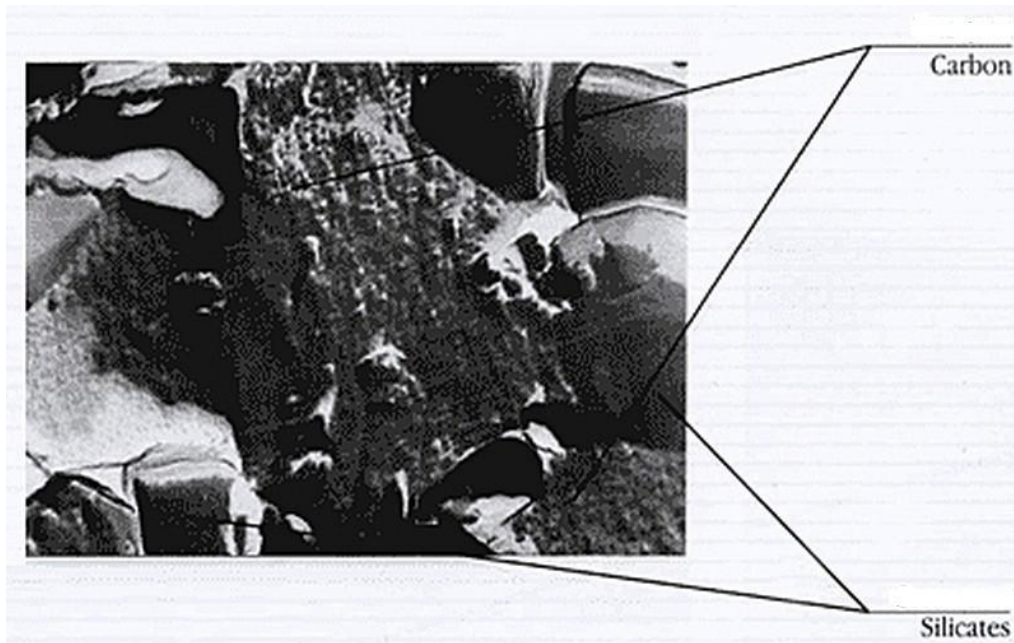


Figure 2. Structure of shungite rock obtained by TEM method. Scanning area  $100 \times 100$  nm, resolution 0.5 nm, magnification 300.000 times. The arrows show the silicate framework of fine dispersed quartz with the size 1–10  $\mu\text{m}$ , and uniformly distributed carbon

The carbonaceous material of shungite is the product of a high degree of carbonization of hydrocarbons. Its elemental composition (% , w/w): C – 98.6–99.6; H – 0.15–0.5; (H + O) – 0.15–0.9 (Golubev, 2000). With virtually constant elemental composition of shungite carbonaceous matter is observed variability in its structure – molecular and supramolecular, as well as surface, and porous structure. X-ray studies showed that the molecular structure of shungite carbon is represented by a solid uncrystallized carbon, which components may be in a state close as to graphite and carbon black and glassy carbon as well, i.e. the maximally disordered (Kovalevski *et al.*, 2001). Carbonaceous matter of shungite having a strongly marked structural anisotropy shows a significant increase in the diamagnetism at low temperatures that is characteristic for fullerenes (Jushkin, 1994).

The basis of shungite carbon compose the hollow carbon fullerene-like multilayer spherical globules with a diameter of 10–30 nm, comprising inclusive packages of smoothly curved carbon layers covering the nanopores (Figure 3). The globule structure is stable relative to shungite carbon phase transitions into other allotropic carbon forms. Fullerene-like globules (the content of fullerenes makes up 0.001%) may contain from a few dozen to a several hundred carbon atoms and may vary in shape and size (Reznikov & Polehovsky, 2000).



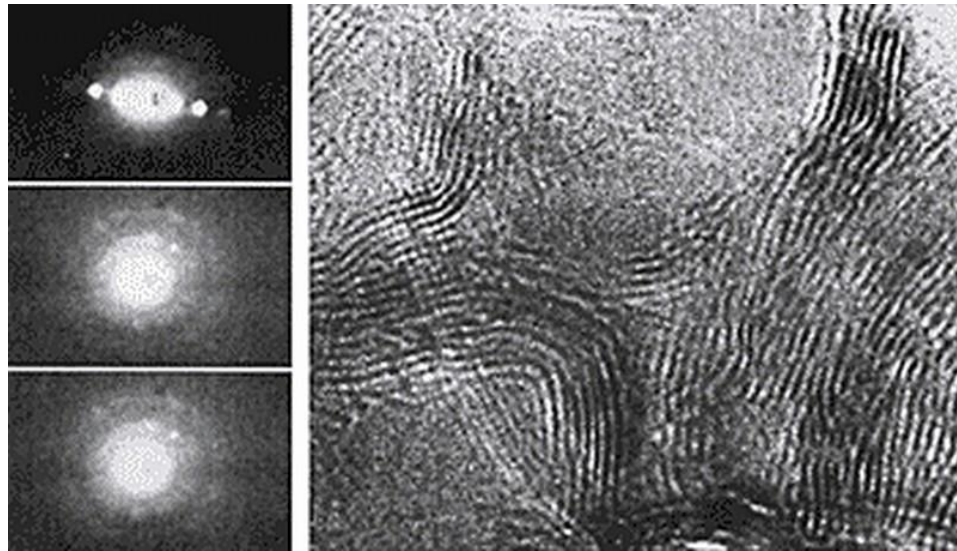


Figure 3. Electron diffraction of nanopattern of shungite carbon in the form of spherical multilayer fullerene globules with a diameter 10–30 nm, obtained by TEM method (probe 0.5–0.7 nm, the energy of the electron beam 100–200 kV, the beam radius 10 nm, the range of the goniometer rotation  $-27 \dots +27^\circ$ ). On the left are shown fluorescent spherical fullerene-like globules, on the right – the multi-layered spherical fullerene-like globules with packets of carbon layers, recorded at a higher resolution

### 3.2. Influence of shungite and zeolite on the deionized water. Mathematical model of shungite and zeolite

By the measurement of IR spectra in the range of vibrations in the crystal mineral framework one can obtain the information: a) on the structure of the framework, particularly type lattice ratio  $\text{SiO}_2/\text{Al}_2\text{O}_3$ , nature and location of cations and changes in the structure in the process of the thermal treatment; b) on the nature of the surface of the structural groups, which often serve as adsorption and catalytically active sites. Other method for obtaining information about the average energy of hydrogen bonds in an aqueous sample is measuring of the spectrum of the water state. It was established experimentally that at evaporation of water droplet the contact angle  $\theta$  decreases discretely to zero, whereas the diameter of the droplet changes insignificantly (Antonov Yuskesseliva, 1983). By measuring this angle within a regular time intervals a functional dependence  $f(\theta)$  can be determined, which is designated by the spectrum of the water state (Antonov Yuskesseliva, 1983; Ignatov, 2005; Ignatov, 2012; Ignatov & Mosin, 2013). For practical purposes by registering the spectrum of water state it is possible to obtain information about the averaged energy of hydrogen bonds in an aqueous sample. For this purpose the model of W. Luck is used, which consider water as an associated liquid, consisted of O–H...O–H groups (Luck *et al.*, 1980). The major part of these groups is designated by the energy of hydrogen bonds ( $-E$ ), while the others are free ( $E = 0$ ). The energy distribution function  $f(E)$  is measured in electron-volts ( $\text{eV}^{-1}$ ) and may be varied under the influence of various external factors on water as temperature and pressure.

For calculation of the function  $f(E)$  experimental dependence between the water surface tension measured

by the wetting angle ( $\theta$ ) and the energy of hydrogen bonds ( $E$ ) is established:

$$f(E) = b f(\theta) / 1 - (1 + b E)^2)^{1/2},$$

where  $b = 14.33 \text{ eV}^{-1}$ ;  $\theta = \arcsin(-1 - b E)$

The energy of hydrogen bonds ( $E$ ) measured in electron-volts (eV) is designated by the spectrum of energy distribution. This spectrum is characterized by non-equilibrium process of water droplets evaporation, thus the term “non-equilibrium energy spectrum of water” (NES) is applied.

The difference  $\Delta f(E) = f(\text{samples of water}) - f(\text{control sample of water})$

– is designated the “differential non-equilibrium energy spectrum of water” (DNES). (Antonov, 1990; Ignatov, 1998)

DNES calculated in milielectron volts (0.001 eV or meV) is a measure of changes in the structure of water as a result of external factors. The cumulative effect of all other factors is the same for the control sample of water and the water sample, which is under the influence of this impact.

The research with NES method of water drops received after 3 days stay with shungite and zeolite in deionized water may also give valuable information on the possible number of hydrogen bonds as percent of water molecules with different values of distribution of energies (Table 4). These distributions are basically connected with restructuring of  $\text{H}_2\text{O}$  molecules with the same energies.

Table 4. Characteristics of spectra of water after 3 day infusion with shungite and zeolite obtained by NES-method

-E(eV) x-axis	Shungite (%((-Evalue)/ (-Etotal value)	Zeolite (%((-Evalue)/ (-Etotal value)	-E(eV) x-axis	Shungite (%((-Evalue)/ (-Etotal value)	Zeolite (%((-Evalue)/ (-Etotal value)
0.0937	2.85	6.3	0.1187	0	12.4
0.0962	8.8	6.3	0.1212	5.9	6.3
0.0987	5.9	0	0.1237	0	0
0.1012	11.8	12.4	0.1262	0	0
0.1037	11.8	6.3	0.1287	0	18.7
0.1062	0	6.3	0.1312	8.8	6.3
0.1087	0	0	0.1337	2.85	0
0.1112	5.9	0	0.1362	0	0
0.1137	11.8	0	0.1387	11.8	2.4
0.1162	11.8	6.3	–	–	–

Another important parameter was measured by the NES method – the average energy ( $\Delta E_{\text{H...O}}$ ) of hydrogen H...O-bonds among individual molecules  $\text{H}_2\text{O}$  after treatment of shungite and zeolite with water to be compiled at -0.1137 eV for shungite and -0.1174 eV for zeolite. The result for control sample (deionized water) is -0.1162 eV. The results with NES method were recalculated by the DNES method. The result of shungite with DNES method is  $0.0025 \pm 0.0011 \text{ eV}$  and for zeolite is  $-1.2 \pm 0.0011 \text{ eV}$ . The results suggest the

restructuring of energy values among H<sub>2</sub>O molecules with a statistically reliable increase of local maximums in DNES-spectra.

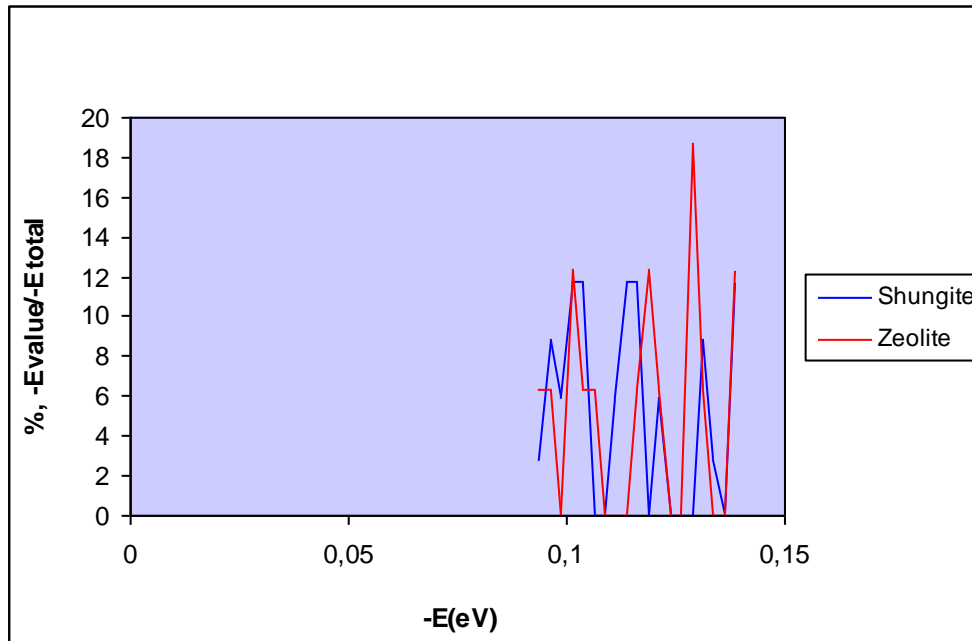


Figure 4. The distribution ( $\%, (-Evalue)/(-Etotal \text{ value})$ ) of water molecules in water solution of shungite/zeolite according to energies of hydrogen bonds ( $-Evalue$ ) to total result of hydrogen bonds energy

There are two conclusions from the DNES spectrums of shungite and zeolite. For the value  $-0.1387 \text{ eV}$  there is local maximums with positive values of shungite and zeolite. Antonov was shown that in the solution with tumor cells there was decreasing of local maximums. Shungite and zeolite make restructuring of water molecules and on molecular level make prophylaxis of development of cancer cells. Antonov was studied that the spectra of solutions containing calcium ions have a local minimum of energy at of  $-0.1 \text{ eV}$  and a local maximum at an  $-0.11 \text{ eV}$ . It was established that the solution of shungite has local minimum of energy at of  $-0.0987 \text{ eV}$  and a local maximum at an  $-0.1137 \text{ eV}$ . The results of shungite are connected with improvement of the conductivity of nervous tissue.

Studies were performed on a 1% solution of blood serum with NES and DNES. Empirical blood serum samples were provided by Kalinka Naneva, Municipal Hospital, Teteven, Bulgaria. The samples were divided into 2 groups of people between 50 and 70 years of age. The first group consisted of people in excellent health. The second group consisted of people in a critical state and suffering from malignant tumors. The average energy of hydrogen bonds among water molecules in the blood serum was examined as a biophysical parameter. The result was obtained as a difference between the spectrum of 1% solution of blood serum (NES) and a control sample with deionized water (NES). This spectrum is DNES. The first group obtained the result  $-9.1 \pm 1,1 \text{ meV}$ , and the second  $-1.6 \pm 1,1 \text{ meV}$ . There is statistical difference between the two groups of results according to the t-criterion of Student at level  $p < 0,05$ . For the control

group of healthy people the value of the spectrum of the largest local maximum is at -0.1387 eV or at a wavelength of 8.95  $\mu\text{m}$ .

The average energy ( $\Delta E_{H...o}$ ) of hydrogen H...O-bonds among individual molecules  $\text{H}_2\text{O}$  was calculated for the water solutions of of shungite and zeolite by NES- and DNES-methods. We studied the distribution of local extremums in water solutions of of shungite and zeolite regarding the energies of hydrogen bonds.

Table 5. Distribution of energies of hydrogen bonds of local extremums in NES and DNES spectrums of water solutions of of shungite and zeolite

-E(eV) x-axis	NES Shungite	NES Zeolite y-axis (eV <sup>-1</sup> )	NES Control sample y-axis (eV <sup>-1</sup> )	DNES Shungite y-axis (eV <sup>-1</sup> )	DNES Zeolite y-axis (eV <sup>-1</sup> )	-E(eV) x-axis	NES Shungite y-axis (eV <sup>-1</sup> )	NES Zeolite y-axis (eV <sup>-1</sup> )	NES Control sample y-axis (eV <sup>-1</sup> )	DNES Shungite y-axis (eV <sup>-1</sup> )	DNES Zeolite y-axis (eV <sup>-1</sup> )
0,0937	11.8	25.0	0	11.8	25.0	0,1187	0	50.0	30.8	-30.8	19.8
0,0962	35.3	25.0	30.8	4.5	-5.8	0,1212	23.5	25.0	30.8	7.3	5.8
0,0987	23.5	0	0	23.5	0	0,1237	0	0	0	0	0
0,1012	47.1	50.0	0	47.1	50.0	0,1262	0	0	30.8	-30.8	-30.8
0,1037	47.1	25.0	30.8	16.3	-5.8	0,1287	0	75.0	0	0	75.0
0,1062	0	25.0	0	0	25.0	0,1312	35.3	25.0	0	35.3	25.0
0,1087	0	0	76.9	-76.9	-76.9	0,1337	11.8	0	30.8	-19.0	-30.8
0,1112	23.5	0	15.4	8.1	-15.4	0,1362	0	0	15.0	-15.0	-15.0
0,1137	47.1	0	30.8	16.3	-30.8	0,1387	47.1	50.0	15.0	32/1	35.0
0,1162	47.1	25.0	61.5	-14.4	-36.5	-	-	-	-	-	-

### 3.3. Results of shungite on mountain water

There is a new parameter in the table 6. This is the local extremum at (-0.1362– -0.1387 eV) (Ignatov, Mosin, 2012). This value is in the spectrum NES as function of distribution according to energy f(E). The norm has a statistically reliable result for blood serum for the control group with people with cancer and the local extremum of f(E) is 24.1 eV<sup>-1</sup>. The function of distribution according to energy f(E) for Teteven tap water is 23.8±1.2 eV<sup>-1</sup>. Table 6 shows the local extremums of different mountain sources, ions of Ca<sup>2+</sup>, Na<sup>+</sup>, Mg<sup>2+</sup>, Fe<sup>2+</sup>, SO<sub>4</sub><sup>2-</sup> and pH.

Table. 6 Mountain sources in Teteven and its ions and pH; \*function of distribution according to energy f(E); function of distribution according to energy f(E) for tap water in Teteven is  $23.8 \pm 1.2 \text{ eV}^{-1}$ . Results of influence of shungite on different sources of mountain water according f(E).

Sources	Ca <sup>2+</sup>	Na <sup>+</sup>	Mg <sup>2+</sup>	Fe <sup>2+</sup>	SO <sub>4</sub> <sup>2-</sup>	pH	local extremum* at (-0.1362 – 0.1387 eV) (1)	local extremum* with shungite (-0.1362 – 0.1387 eV) (2)	difference between (2) and (1)
	mg/ dm <sup>3</sup> norm (<150)	mg/ dm <sup>3</sup> norm (<200)	mg/ dm <sup>3</sup> norm (<80)	mg/ dm <sup>3</sup> norm (<200)	mg/ dm <sup>3</sup> norm (<250)	norm (6.5-9.5)	eV <sup>-1</sup> norm (>24.1)	eV <sup>-1</sup> norm (>24.1)	eV <sup>-1</sup> norm (>24.1)
Deionized water							<b>15.4</b> <b>±0.8</b>	<b>47.1</b> <b>±2.8</b>	<b>31.7</b> <b>±1.6</b>
1. Klindiovo	89.9 ±9.0	4.1 ±0.4	6.98 ±0.7	40.2 ±4.0	17.7 ±1.8	8.0 ±0.1	<b>44.4</b> <b>±2.2</b>	<b>63.2</b> <b>±3.2</b>	<b>18.6</b> <b>±0.9</b>
2. Gorna cheshma	103.6 ±10.4	4.2 ±0.4	15.5 ±1.6	9.6 ±0.96	89.9 ±9.0	7.3 ±0.1	<b>51.6</b> <b>±2.6</b>	<b>80.0</b> <b>±4.0</b>	<b>28.4</b> <b>±1.4</b>
3. Dolna cheshma	94.4 ±0.94	2.5 ±0.3	12.10 ±1.21	9.0 ±0.9	15.99 ±1.60	7.9 ±0.1	<b>34.2</b> <b>±1.7</b>	<b>51.6</b> <b>±2.6</b>	<b>17.4</b> <b>±0.9</b>
4. Sonda	113.6 ±11.4	7.3 ±0.7	15.99 ±1.60	5.00 ±0.5	57.2 ±5.7	7.3 ±0.1	<b>54.4</b> <b>±2.7</b>	<b>70.6</b> <b>±3.5</b>	<b>16.2</b> <b>±0.8</b>
5. Ignatov izvor	40.44 ±4.04	0.6240 ±0.624	2.46 ±0.25	13.0 ±1.4	17.9 ±1.8	6.82 ±0.1	<b>48.0</b> <b>±2.4</b>	<b>85.7</b> <b>±4.3</b>	<b>37.7</b> <b>±1.9</b>
6. Gechovoto	66,0 ±6.0	1.46 ±0.15	2,1 ±0.2	11,4 ±1.1	15,9 ±1.6	7.94 ±0.1	<b>41.7</b> <b>±2.1</b>	<b>84.2</b> <b>±4.2</b>	<b>42.5</b> <b>±2.1</b>

There are new data for the influence of shungite on the spectrum of different mountain sources (Table 6). The results are on the local extremum at (-0.1362– -0.1387 eV). There is tendency the increasing of local extremums in solution of shungite in water regarding the same mountain water as control sample. The dependence of local extremums at (-0.1362– -0.1387 eV) is inversely than contain of ions in water for

difference at (-0.1362– -0.1387 eV) of solution of shungite in mountain water and the same water as control sample. The research will continue with new experiments.

### 3.4. Shungite as absorbent

Owing to the unique porous structure the natural minerals shungite and zeolite are ideal absorbents and fillers (Gorshteyn *et al.*, 1979), and as sorbents have a number of positive characteristics:

- High adsorption capacity, characterized by low resistance to water pressure;
- Mechanical strength and low abrasion resistance;
- Corrosion-resistance;
- Absorption capacity relative to many substances, both organic (oil, benzene, phenol, pesticides, etc.) and inorganic (chlorine, ammonia, heavy metals);
- Catalytic activity;
- Relatively low cost;
- Environmental friendliness and ecological safety.

According to the data on adsorption capacity shungite loses effectiveness before the activated carbon filter in the first stage of filtration, during the first 24 h, further shungite began purified water with a high and constant speed. This is explained by high catalytic properties of shungite and its ability to catalytically oxidize organic substances adsorbed on the surface. The mechanism of interaction of shungite with water has not been completely understood. It is assumed that shungite can adsorb oxygen actively interacting with them as a strong reducing agent in water and in air (Cascarini de Torre *et al.*, 2004). In this process is produced atomic oxygen, which is a strong oxidizing agent oxidizing adsorbed on shungite organic substance to CO<sub>2</sub> and H<sub>2</sub>O, thus, freeing the surface of shungite for new acts of adsorption. Overexposure of shungite in respect to dissolved metal cations in water as Ca<sup>2+</sup>, Mg<sup>2+</sup>, Fe<sup>2+</sup> and Fe<sup>3+</sup> is explained by the fact that the metals are transferred by the catalytically active shungite into the form of insoluble carbonates due to the oxidation of organic matter to CO<sub>2</sub>.

The research of antioxidant properties of shungite in relation to organochlorine compounds, and free radicals have shown that shungite removes free radicals out of water in 30 times more effective than activated carbon (Mosin & Ignatov, 2013b). This is a very important factor, because the free radicals formed during water treatment with chlorine and its derivatives, have a negative impact on the human health that is the cause of many diseases (cardiovascular diseases, cancer, etc.).

These positive qualities allow using shungite as an effective filter material for wastewater treatment and purification from organic and chlorinated organic substances (oil, pesticides, phenols, surfactants, dioxins, etc.). Thus shungite is able to purify wastewater from oil up to threshold limit value (TLV) of water discharge into the water reservoir. Shungite adsorbs on its surface up to 95% of contaminants, including organochlorine compounds, phenols, dioxins, heavy metals, radionuclides, etc., removes turbidity and color, and gives the water good organoleptic qualities, additionally saturating it with micro- and macro-elements (Table 7). Thus, adsorption activity of shungite relative to phenol makes up 14 mg/g, while for thermolysis resins – 20 mg/g, for oil products – more than 40 mg/g. Model experiments showed that heavy metals (copper, cadmium, mercury, lead), boron, phenol and benzene contained in water in concentrations being

in 10–50 times higher than the TLVs, after the treatment by shungite in stationary or dynamic conditions on the shungite filter units, the content of these pollutants in water is reduced below the established levels of regulatory documents. In this case into the water does not enter any toxic elements from shungite adsorbents.

Table 7. Indicators of performance of filters based of mineral shungite

№	Common water pollutants	The removal degree, %
1	Fe <sup>2+</sup> /Fe <sup>3+</sup>	95
2	Zn <sup>2+</sup>	80
3	Pb <sup>2+</sup>	85
4	Cu <sup>2+</sup>	85
5	Cs <sup>2+</sup>	90
6	St <sup>2+</sup>	97
7	Radionuclides	90
8	Fluorine	80
9	Ammonia	90
10	Chlorine and organochlorine compounds	85
11	Phenols	90
12	Dioxins	97
13	Helminth's eggs	90
14	Smell	85
15	Turbidity	95

In addition, owing to adsorption activity of shungite against pathogenic microflora shungite has strong bactericidal properties that allow carrying out the efficient disinfection of drinking water by this mineral in water treatment and water purification technologies. It is observed the bactericidal activity of shungite against pathogenic saprophytes and Protozoa. There is evidence that after the passage of water containing bacterium *E. coli*, through shungite filter there is an almost complete removal of this bacterium (the viral titer varies from 2300 cells /l in initial water up to 3 cells/l in treated water) (Mosin & Ignatov, 2012). Of 1785 cells/l of protozoa (ciliates, rotifers and crustaceans) contained in the initial water after the treatment by shungite were observed only a few exemplars (5 cells/l). In addition to these qualities, shungite has biological activity.

Owing to all these positive properties shungite may find its application for the preparation of drinking water in flow-through systems of any capacity for industrial and domestic purposes, as well as in the wells in order to improve the quality characteristics of water to return water its beneficial properties.

Especially effective and technologically justified is the use of complex filter systems based of the mixtures of shungite with activated carbon or zeolite, with subsequent regeneration of the absorbents (Podchaynov, 2007). When adding to the treatment scheme to shungite other natural absorbents (zeolite, dolomite,



glaucanite) purified water is enriched to physiologically optimal levels by calcium, magnesium, silicon and sodium ions.

#### 4. Conclusions

The fullerene-containing natural mineral shungite and microporous crystalline aluminosilicate mineral zeolite can find wide practical applications in many branches of science and industry, and can be used as an alternative to activated carbon the natural mineral absorbent in water treatment. Efficiency of using these two natural minerals is stipulated by the high range of valuable properties (absorption, catalytic, antioxidant, regenerative, antibacterial), high environmental safety and relatively low cost of filters based on shungite and zeolite as well as existence of the extensive domestic raw material base of shungite and zeolite deposits. All these factors contribute to the further expansion of these minerals and a big variety of materials based on it. There is tendency the increasing of local extremum between solution of shungite in water and the same water us control sample is inversely than contain of ions in water. The research will continue with new experiments.

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