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A giant Palaeoproterozoic deposit of shungite in NW Russia: genesis and practical applications

V.A. Melezhik[a,*], M.M. Filippov[b], A.E. Romashkin[b]

[a] Geological Survey of Norway, Stratigic Research and Development, Leiv Eirikssons vei 39, N-7491, Trondheim, Norway
[b] Institute of Geology, Karelian Science Centre, Pushkinskaya 11, 185610, Petrozavodsk, Russia

Abstract

Occurrences of 2.0 Ga, mature organic material from the Lake Onega area, NW Russia, constitute one of the most remarkable accumulations of organic carbon from the Palaeoproterozoic. The deposit occurs in a 1000-m sedimentary-volcanic succession developed over an area of 9000 km^2 with an estimated total carbon reserve exceeding 25×10^{10} tonnes. The organic material occurs in the form of the mineraloid, shungite, which is a black, non-crystalline, semi-metallic material that contains >98 wt.% C.

The shungite-bearing rocks were accumulated within a volcanic continental rift setting, in a non-euxinic, brackish-water, lagoonal environment developed on the rifted margin of the Archaean craton. The occurrences of shungite-bearing rocks represent a combination of a petrified oil field, petrified organosiliceous diapirs and oil spills. These are exemplified by three types of deposit: (i) in situ stratified, (ii) migrated diapirs and (iii) redeposited clastic. In situ stratified deposits are composed of metamorphosed oil shales (< 50 wt.% C), rocks containing autochthonous kerogen residue and allochthonous organic matter (50–75 wt.% C) and migrated bitumen, originally liquid hydrocarbons (>80 wt.% C). Diapiric deposits form non-stratified, cupolas or mushroom-shaped bodies composed of shungite containing 35–75 wt.% SiO_2 and 20–55 wt.% C. These are considered to represent organosiliceous rocks, originally gels or mud. The shungite rocks show abundant shrinkage cracks, cryptic fluidal textures and brecciation caused by multiple fluidisation processes. The current data are consistent with either diapiric or mud-volcanic origins. Occurrences of clastic shungite are hosted by lacustrine volcanoclastic greywackes deposited from turbiditic flows. Shungite occurs in rocks as < 1 mm to 20 cm clasts of lustrous shungite that probably represent redeposited, oxidised oil derived from oil spills.

Shungite has a heterogeneous molecular structure in which carbon occurs as 10 nm globules irregularly distributed within carbon showing no structure. The unusual physicochemical and structural properties of shungite are used in diverse industrial and environmental applications including metallurgy, water purification, thermolysis and organosynthesis of cyclic hydrocarbons. Shungite is an effective sorbent for removal of organic and inorganic substances, pathogenic bacteria and heavy metals from contaminated water.

Keywords: Karelia; Palaeoproterozoic; Shungite; Organic matter; Hydrocarbon

1. Introduction

Occurrences of autochthonous, mature, organic coal-like material from the Onega area (Melezhik et

* Corresponding author. Tel.: +47-73-90-4011; fax: +47-73-92-1620.
E-mail address: victor.melezhik@ngu.no (V.A. Melezhik).

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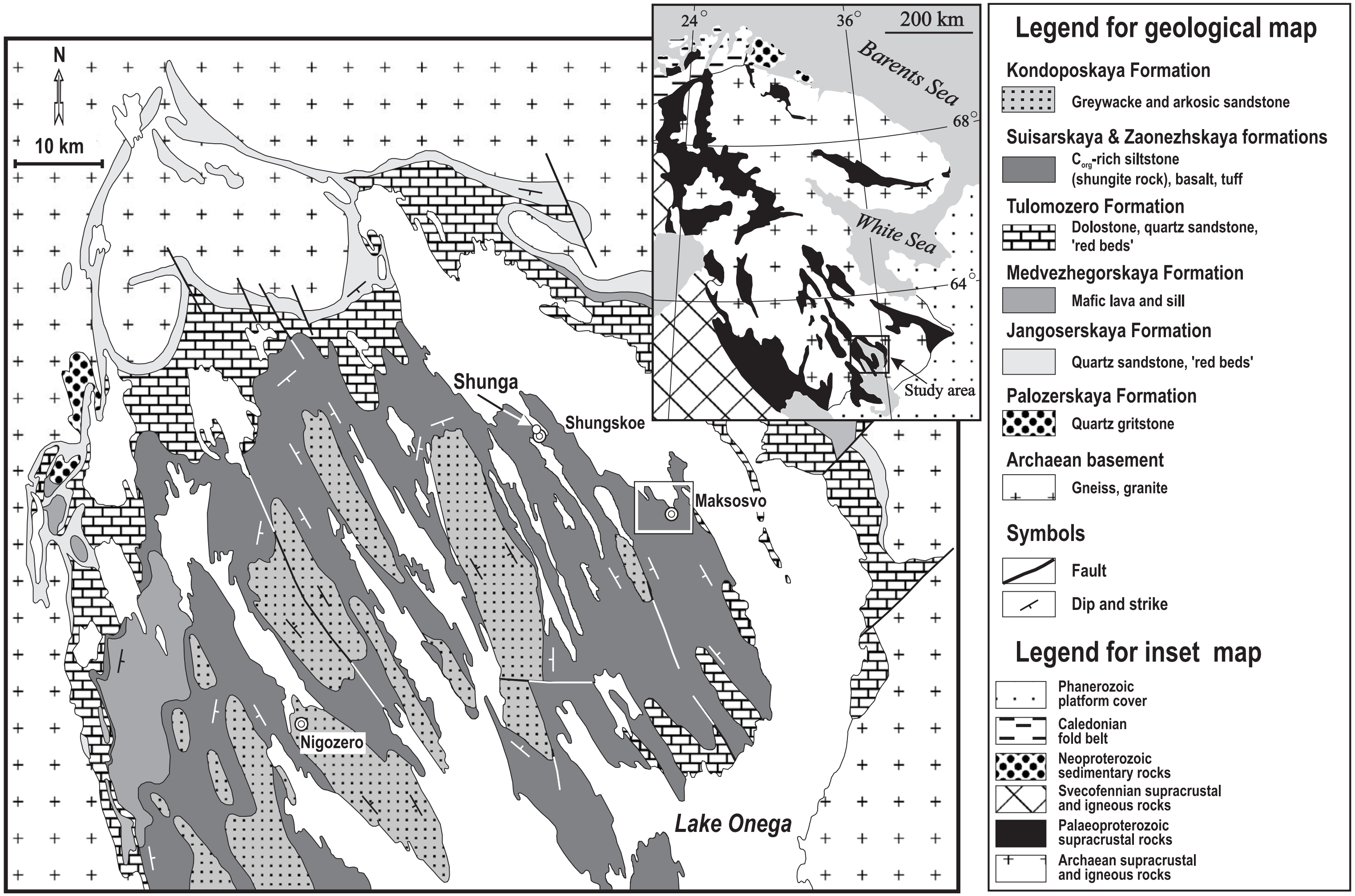


Fig. 1. Geographical location and geological map of the northern Lake Onega area (simplified after Akhmedov et al., 1993). The symbol for the Tulomozero carbonate rocks does not show orientation of bedding. White outlines indicate the position of the Tolvuya synform shown in detail in Fig. 2.

al., 1999) together with pyrobitumens from the Franceville Series, southeastern Gabon (Nagy et al., 1991, 1993), represent the greatest accumulations of organic carbon reported to date from Palaeoproterozoic sequences. In the Onega area, near the Karelian village of Shunga NW Russia, the organic matter is represented by a non-crystalline and non-graphitized form of carbon, shungite, which has puzzled geologists since the 18th century.

Numerous Russian publications on shungite exist (e.g., Borisov, 1956; Firsova and Yakimenko, 1985; Filippov, 1994a,b, 2000, 2002 and references therein) and some have been translated into English (e.g. Volkova and Bogdanova, 1986; Ivankin et al., 1987). Few articles on shungite, however, exist in western journals (e.g., Khavari-Khoransani and Murchison, 1979; Buseck et al., 1998). In a previous contribution, we considered depositional environments and the nature of shungite carbon based on sedimentological and isotopic evidence (Melezhik et al., 1999). The goals of this paper are to cover (i) the characteristics of shungite, (ii) an overview of the main deposits of shungite, (iii) practical applications of shungite and shungite-bearing rocks and (iv) the economic significance and future potential of shungite.

2. Definitions and terminology

During the course of 200 years of investigation, the various definitions of the term shungite have led to misunderstandings and confusion. The term was originally introduced by Inostranzev (1879) to describe a black, lustrous substance containing ca. 98 wt.% C that occur in the form of veins and layers near Shunga (Fig. 1). Later, optical, geochemical and genetic classifications of shungite and shungite-bearing rocks were introduced, as reviewed by Filippov (2000, 2002). Borisov (1956) classifies shungite and shungite-bearing rocks by their carbon content. However, his terms, shungite-1 (98–100 wt.% C), shungite-2 (35–80 wt.% C), shungite-3 (20–35 wt. %C), shungite-4 (10–20 wt.% C) and shungite-5 (<10% wt.% C), do not distinguish between shungite and shungite-bearing rocks. Moreover, this widely accepted classification lumps together shungite-bearing rocks, which may have contrasting compositions and lithologies. Shungite-5, for example, may be represented by tuff, dolostone, limestone, chert, basalt or even gabbro.

Strictly speaking, shungite is not a mineral because it is amorphous (Yushkin, 1995). The term shungite should be restricted to a black, lustrous mineraloid having $=98$ wt.% C, whereas shungite-bearing rocks should be specified by their composition and lithology with the prefix 'shungite', e.g., shungite-bearing dolostone.

Shungite occurs in both disseminated and in pure forms in sedimentary and volcanic rocks as well as in veins. All types of shungite are also found in younger sedimentary rocks as clasts. The dispersed form, occurring as an impregnation in various rocks, represents bulk shungite. Pure lustrous shungite (>98 wt.% C_{org}) is rare, forming less than 1 vol.% of the shungite occurrence thus will probably be formed as a result of mobilisation of liquid hydrocarbons and is referred to as *migrated shungite*.

The term *layer-shungite* is used to describe migrated forms of lustrous shungite occurring either as a layer or a lens that is conformable or sub-conformable with the bedding of the host rocks. In contrast, the term *vein-shungite* is used to describe migrated forms of lustrous shungite in veins that clearly cut the host-rock bedding. Additionally, migrated lustrous shungite cements fragments and fills voids in intensively brecciated shungite, and fills vesicles in basalts.

3. Geology and stratigraphy of the northern Onega Lake area

Lake Onega is located in the southeastern margin of the Fennoscandian Shield (Fig. 1), where the Palaeoproterozoic sedimentary succession consists of a platformal sequence. The sequence lies on Archaean granites and gneisses with a first-order unconformity, marked in several localities by well-developed regoliths (e.g., Heiskanen, 1987). The Palaeoproterozoic rocks dip 10–50° and fill a large, NW-trending synform, which is covered by Palaeozoic platformal sediments south of Lake Onega (Fig. 1).

The Palaeoproterozoic succession of the Lake Onega area includes seven lithostratigraphic units though shungite occurs only in the Zaonezhskaya, Suisarskaya and Kondopozhskaya formations (Fig. 2). The main concentrations of shungite are confined to

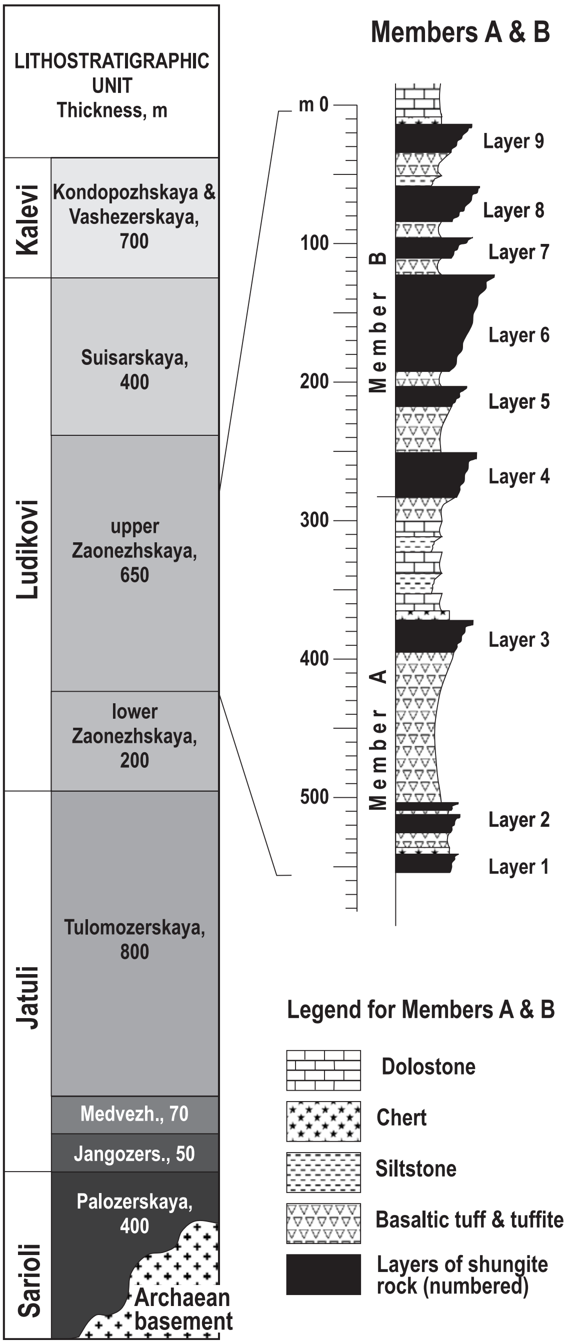


Fig. 2. Lithostratigraphic subdivisions of the northern Lake Onega area and position of shungite layers.

nine layers with thicknesses from 5 to 120 m within the Zaonezhskaya Formation with the lowermost numbered as Layer 1 and uppermost as Layer 9 (Fig. 2). The thickest zone, Layer 6, hosts several shungite deposits and is therefore also known as the 'Productive Horizon'. This particular layer has been intensively drilled and studied during exploration and prospecting in the 1960s.

Low-C_{org} rocks in the Kondopozhskaya Formation rest unconformably on the Suisarskaya Formation and contain beds with abundant clasts of the underlying Suisarskaya Formation volcanites and Zaonezhskaya Formation shungite-bearing rocks.

The whole Palaeoproterozoic sequence was deformed and underwent greenschist facies metamorphism during the 1.8-Ga Svecofennian orogeny. A gabbro intrusion from the upper part of the Suisarskaya Formation yields a Sm–Nd age of 1980 ± 27 Ma (Pukhtel et al., 1992), which provides an upper age limit for the Zaonezhskaya succession. The lower age limit is constrained by a Pb–Pb age of 2090 ± 70 Ma (Vasil'eva et al., 2000) obtained from underlying Tulomozero dolostones.

4. Main deposits of shungite rocks

In the Lake Onega area, sedimentary and volcanoclastic formations highly enriched in organic carbon are developed over an area of 9000 km^2 (Fig. 1). A total carbon reserve was estimated over 25×10^{10} tonnes with the cut-off of ca. 2 wt.% C (Galdobina, 1993). Although numerous occurrences of shungite-rich rocks are known in the area only the Maksosvo, Zazhogino and Nigozero deposits have economic significance. The Shungskoe deposit is mainly of scientific rather than economic interest because only a limited amount of ore remains from mining in the 1930s. The Maksosvo, Zazhogino and Shungskoe deposits are stratigraphically confined to the upper part of the Zaonezhskaya Formation, whereas the Nigozero deposit is confined to the Kondopozhskaya Formation (Fig. 2).

All deposits and occurrences of shungite and shungite-bearing rocks of the Lake Onega area can be classified into three main genetic groups, namely (i) in situ stratified (Shungskoe type, see Fig. 3), (ii) migrated diapirs (Maksosvo type) and (iii) redeposited

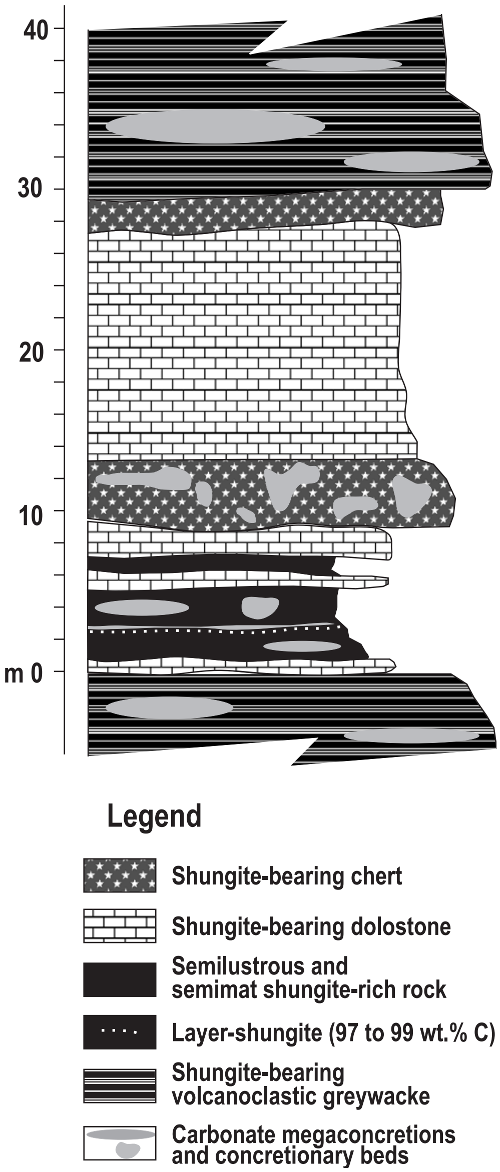


Fig. 3. Composite lithological section of the Shungskoe deposit.

clastic (Nigozero type). Typical textures of shungite and shungite rocks can be seen in Figs. 4 and 5.

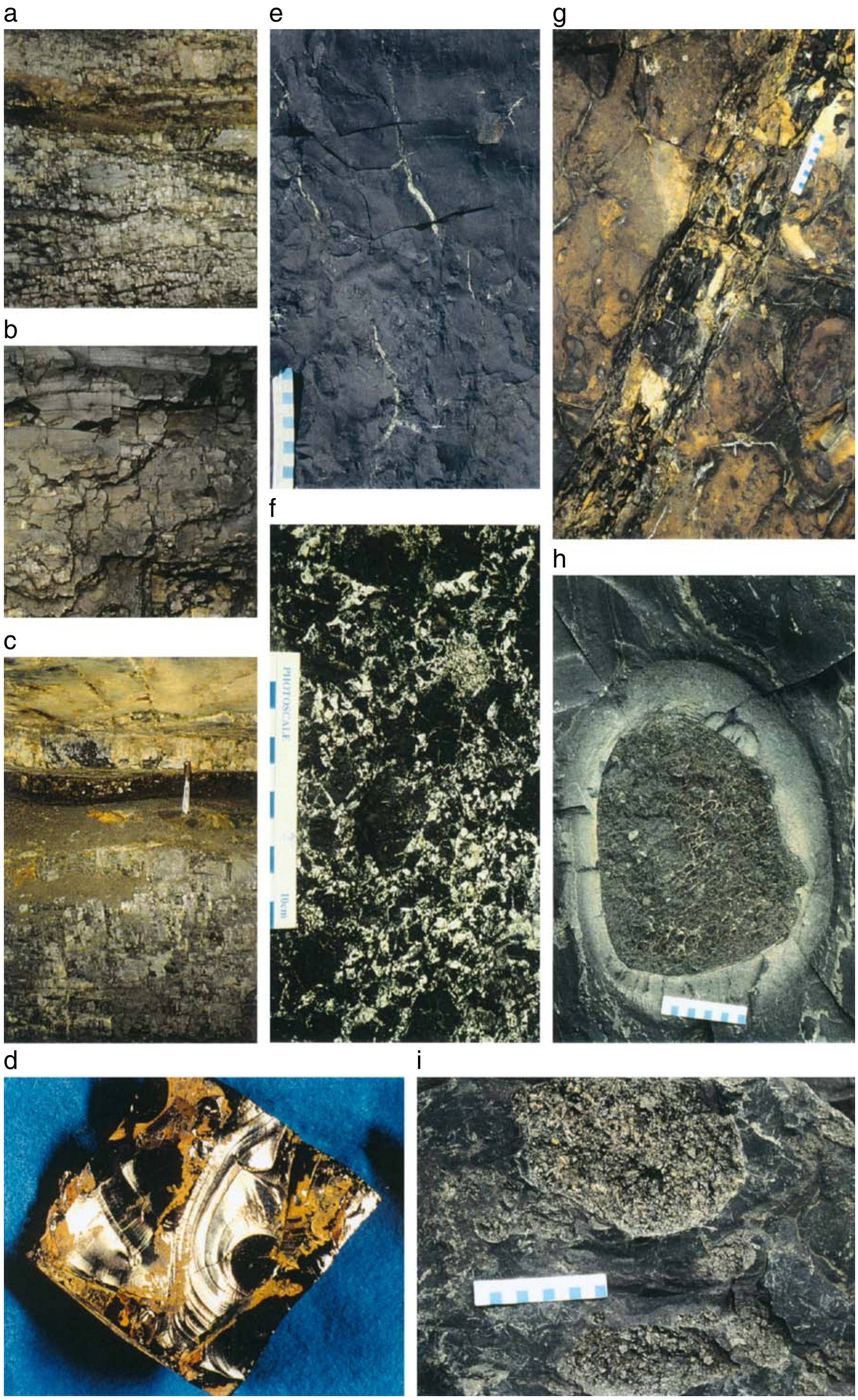
4.1. In situ stratified deposits

A typical representative of the in situ stratified shungite deposits is the Shungskoe deposit located near the small village of Shunga (Fig. 1) that has been well known since the 1800s. The deposit was mined in the 1930s. The exact stratigraphic position of the deposit remains unknown, but is thought (e.g., Filippov, 1994a) to have been confined to Layer 9 (Fig. 2). The succession hosting the deposit exhibits shallow dips (0–35°) and fills a small, closed, NW-trending synform. Although all rocks at Shunga are enriched in shungite, several seams have particularly large shungite concentrations (Fig. 3). The Shungskoe deposit also contains the thickest known development of the remobilised form of shungite, mostly in the form of layers. The semimat, semilustrous and lustrous, coal-like rocks, as well as layer- and vein-shungite, are interbedded with chert and dolostone, and are collectively sandwiched between bedded and laminated shungite tuffs and volcanoclastic siltstones and greywackes (Fig. 3).

Two adits driven in the 1930s intersect a 4.5-m-thick, slightly deformed, subhorizontal stratum composed of semimat and semilustrous shungite-rich rocks as well as layer-shungite. The bed has been traced by underground workings over a distance of 50 m. Up to 10 semimat and semilustrous shungite rock seams, 20–100 cm thick, have been observed in dolostone near Shunga. Lenses and beds of concretionary carbonates are abundant within semimat and semilustrous shungite rocks as well as within overlying cherts, but black dolostones and the cherts contain less than 2 wt.% C_{org} (Melezhik et al., 1999).

4.2. Semimat and semilustrous shungite rocks

The seams of semimat and semilustrous shungite rocks are conformable with the stratigraphy and have transitional contacts with shungite siltstones and greywackes, but their boundaries with cherts and dolostones are always sharp. The semilustrous variety is black with a grey hue and is either weakly laminated or massive with vitreous lustre and a conchoidal fracture with a well developed parting (Fig. 4a). The semimat shungite rocks exhibit less pronounced partings (Fig. 4b). Commonly, rocks containing >50 wt.% C_{org} do not exhibit primary lamination (Melezhik et al., 1999). The poorly developed lamination can be observed when rocks contain greater amounts of pyrite and siliciclastic material. Semilustrous and semimat shungite rocks contain 57–64 wt.% C_{org} (Table 1) and exhibit a lensoidal microtexture and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syneresis cracks that can be observed only on a microscale (Fig. 5a,b).

4.3. Layer-shungite

The remobilised form of shungite (>98 wt.% C_{org}, Table 1) documented at the Shunga mine occurs either as layer-shungite, vein-shungite, or as spherical and lensoidal inclusions. In all cases, layer-shungite appears where the primary bedding has been disturbed by faulting (Kryzhanovsky, 1931). The layer-shungite is most abundant in the uppermost seams of semimat and semilustrous shungite rocks, as well as along the contact with the upper dolostone lens. The layer-shungite always shows sharp contacts with all rocks including the semilustrous and semimat varieties (Fig. 4c). The layer-shungite at the Shunga mine has a maximum thickness of 62.5 cm (Kontkevich, 1878). The 15-cm-thick layer-shungite sampled in the adit is a homogeneous, massive and black to brown-black substance with conchoidal fracture and no visible internal lamination (Fig. 4d). The layer-shungite exhibits no microtexture and is composed of nearly pure homogeneous organic matter with only traces of detrital material and tiny grains of pyrite.

4.4. Migrated diapir shungite deposits

A typical representative of the diapir shungite deposits is the Maksovo deposit (Fig. 1). The deposit was prospected in the 1960s and is not currently being exploited. The deposit is confined to Layer 6 (Fig. 6, Profiles A–B and C–D) and structurally forms an asymmetrical, cupola-shaped body. The deposit has an ellipsoidal outcrop pattern with axes of 700 and 500 m (Fig. 6) with most shungite occurring in the dispersed form. Prospected reserves of the shungite-bearing rocks are 33 million tonnes. The C_{org} content of the deposit ranges between 25 and 55 wt.%, with 14.3% rocks containing <26 wt.% C_{org} and 27.5% containing >35 wt.% C_{org}.

The orebody consists mainly of massive, jointed and brecciated, highly siliceous shungite rocks (Table 1) within the core of a small antiform. Although the spatial distribution of the massive and brecciated rocks is complex, the massive variety is mainly associated with the footwall of the orebody (Fig. 6, Profile E–F). The shungite rocks contain dolomitic megaconcretions as well as fragments of massive black dolostones. Beds of laminated black dolostone embedded in dolomite-cemented volcanoclastic greywacke occur in the footwall of the orebody. Cherts are abundant in the country rocks but not in the orebody. Both diagenetic and sedimentary dolostones as well as cherts contain shungite, but the C_{org} content is commonly <2 wt.% (Melezhik et al., 1999).

The greatest thickness of the orebody is 100–120 m though it decreases to less than 35 m towards the periphery of the cupola (Fig. 6). The massive and brecciated shungite rocks are gradually replaced towards the margins of the orebody by weakly laminated rocks containing less shungite. The bedding and lamination are pronounced when the shungite content is well below 20 wt.%.

Country rocks consist of basaltic tuff, volcanoclastic siltstone, greywacke, dolostone, limestone, chert intruded by gabbro sills. All the rocks contain variable amounts of shungite. Those located beneath the shungite orebody are enriched in carbonate minerals.

Fig. 4. Major types of shungite and shungite-bearing rocks. (a) Semilustrous shungite rock with well-developed parting from the Shungskoe underground mine. Width of photograph = 1 m. (b) Semimat shungite rock with weak parting. Note poorly developed lamination in the upper part where the rock contains higher abundances of siliciclastic material. Shungskoe underground mine. Width of photograph = 1 m. (c) Lustrous layer-shungite (dark brown) sandwiched between a lens of diagenetic dolostone (light grey, above) and semilustrous shungite rock (beneath). Dolomite concretion is located beneath the layer of lustrous shungite (beneath 25 cm knife). Shungskoe underground mine. (d) Lustrous layer-shungite made up of 98.4 wt.% C_{org} with jarosite films (brown) from the Shungskoe underground mine. Width of specimen = 5 cm. (e) Massive shungite rock from the Maksovo deposit. 10 cm scale bar. (f) Quartz-cemented shungite rock breccia from the Maksovo deposit. 10 cm scale bar. (g) Vein-shungite cross-cutting semimat shungite rocks. Vicinity of the Maksovo deposit. 10 cm scale bar. (h) Disc-like inclusion of lustrous shungite (pyrobitumen or anthraxolite) spread along the bedding surface of thinly laminated Kondopozhskaya siltstones. Shungite ‘disc’ is intensively jointed as a result of shrinkage. The photograph was taken from the Nigozero quarry. 10 cm scale bar. (i) Several clasts of lustrous shungite in the matrix-supported conglomerate of the Kondopozhskaya Formation. The photograph was taken from the Nigozero quarry. 10 cm scale bar.

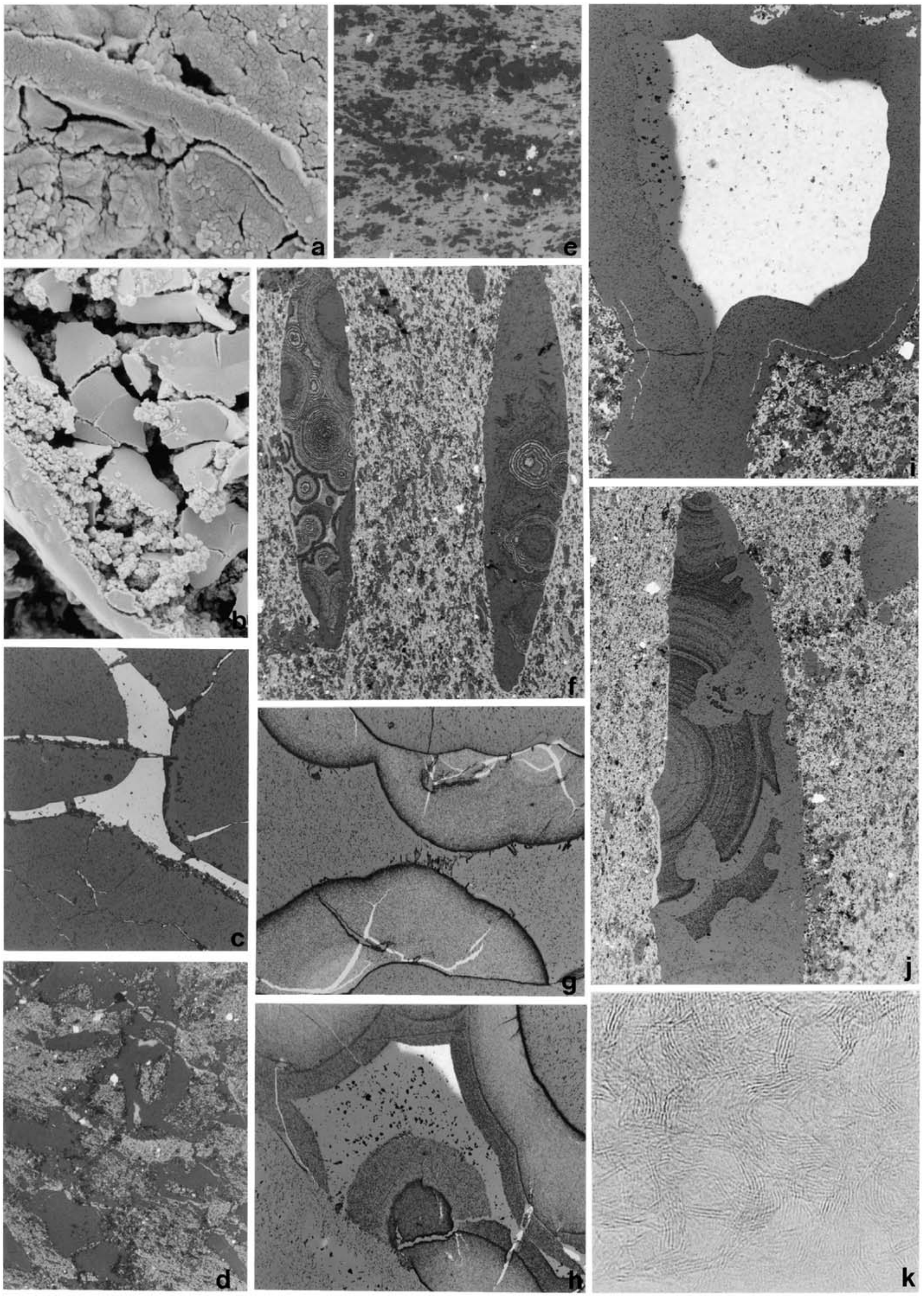
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Table 1
Chemical composition of shungite rocks and shungite from major deposits in the Onega Lake area, Russian Karelia (data are from Filippov, 1994a,b; Melezhik et al., 1999)

Sample nn	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	MgO	CaO	Na_2O	K_2O	MnO	P_2O_5	S	TOC
Shungskoe deposit												
1	–	5.74	10.94	0.55	1.23	0.31	0.25	3.06	–	0.05	5.0	64.1
2	15.19	5.43	9.60	0.44	0.88	0.16	–	2.09	–	0.04	3.8	56.7
3	0.32	0.23	0.13	–	0.03	0.11	0.21	0.11	n.d.	n.d.	0.2	98.4
Maksovo deposit												
4	52.61	2.71	0.24	0.23	0.42	0.10	–	0.74	–	0.06	0.1	37.7
5	57.56	2.97	0.15	0.21	0.35	0.10	–	0.81	–	0.05	–	35.5
6	0.26	0.53	1.02	0.002	–	0.28	–	0.02	0.02	–	n.d.	96.3
Nigozero deposit												
7	51.27	17.74	13.84	2.23	2.67	1.17	2.50	2.71	0.09	0.15	–	0.9

Shungskoe deposit: (1) semilustrous shungite rock, (2) semimat shungite rock, (3) layer-shungite. Maksovo deposit: (4, 5) brecciated shungite rock, (6) vein-shungite. Nigozero deposit: (7) laminated, shungite-bearing siltstone.
n.d., not determined; dashes, below detection limit. Detection limits are as follows: SiO_2-0.2; Na_2O, S-0.1; TiO_2, K_2O, MnO-0.01.

Regardless of their lithological characteristics, shungite rocks of the Maksosvo deposit are composed of two basic components (Table 1). These are 35–75 wt.% silica in the form of cryptocrystalline quartz or an amorphous silica (Filippov et al., 1998) and 20–55 wt.% C_{org} in the form of shungite (Filippov, 1994a). As detrital quartz has not been observed in the shungite rocks, they are considered to represent silica-shungite substances, originally organosiliceous gel or mud. All types of shungite rocks contain minor pyrite as syngenetic recrystallised framboids, diagenetic layers and concretions as well as porphyroblasts and joint fillings (Shatzky, 1990), but the total sulfide contents are commonly low such that typical C/S ratios range from 6 to 1000 (20 on average, Melezhik et al., 1999).

4.5. Massive shungite rocks

Massive black and dark grey, mat and cryptocrystalline shungite rocks (Fig. 4e) form the core of the Shungskoe orebody (Fig. 6, Profiles A–B and C–

Fig. 5. Microstructure of shungite. (a) Scanning electron microscope (SEM) image showing open syneresis cracks (black) developed in shungite that fills vug. Shungskoe underground mine. Photograph width = 10 μm. (b) SEM image showing intensive syneresis cracking, which results in the collapse structure. Note that platy shungite fragments are partly 'welded' by growing cauliflower-like clusters of shungite. Shungskoe underground mine, photograph width = 9 μm. (c) Photomicrograph taken under reflected light demonstrates quartz-filled cracks (white) in globular shungite. The Maksovo deposit. Photograph width = 4 mm. (d) The structural organisation of 'cryptic' breccia from the Maksovo deposit. Note chaotic dispersion of the dark grey shungite fragments in the pale grey shungite matrix showing fluidal structure. Reflected light, photograph width = 8 mm. (e) Shungite rock with 'cryptic structural heterogeneity' from the Maksovo deposit. The pale grey shungite matrix exhibiting heterogeneity, which is expressed by the micron-size, dark grey shungite fragments 'floating' in the pale grey shungite. Note preferential orientation of small dark grey shungite particles emphasising the fluidal structure. Reflected light, photograph width = 0.1 mm. (f) Elongated, rice grain-shaped fragments of shungite with micron-scale concentric structure from the Maksovo deposit. Reflected light, photograph width = 0.5 mm. (g) Photomicrograph showing small shrinkage vug, which is filled with globular and massive shungite in shungite rock from the Maksovo deposit. Note thin syneresis cracks healed by quartz (white). Reflected light, photograph width = 3 mm. (h) The large vug is filled with globular shungite in vuggy shungite rocks from the Maksovo deposit. Note that concentric rings are distinguished by pale grey and grey colour patterns emphasising the growth feature. The white 'triangle' is composed of SiO_2. Reflected light, photograph width = 5 mm. (i) The large gas-escape (?) vug with zoned infill in vuggy shungite rock from the Maksovo deposit. The walls are lined with globular shungite whereas the core is filled with quartz. Reflected light, photograph width = 8 mm. (j) Photomicrograph of shungite fragment with concentric structure form the Maksovo deposit. Note that the concentric system is delicately eroded by a later generation of shungite. Reflected light, width of photograph = 0.2 mm. (k) High-resolution transmission electron microscopy image of the shungite carbon. Stripes represent atomic layers of carbon (from Kovalevski and Melezhik, 2000). Photograph width = 20 nm.

D). The rocks are opaque in transmitted light. The shungite content ranges between 30 and 49 wt.%. X-ray diffractometry suggests that the shungite-free mass is mainly composed of quartz with subordinate sericite, calcite, chlorite and feldspar (Filippov, 1994a). In places, massive shungite rocks exhibit a cryptic structural heterogeneity expressed by the chaotic dispersion of millimetre- to centimetre-size, elongated, angular and flame-shaped, dark grey shungite fragments in a pale grey heterogeneous matrix, resulting in the development of flaser-like and fluidal structures. The matrix heterogeneity is caused by dispersion of micron-size, elongated, rounded, dark grey shungite fragments in a pale grey shungite framework. The latter may contain micron-size particles and pyrite crystals. The pale grey shungite matrix resembles a lithified liquid, which fills all joints and open spaces in dark grey shungite fragments. These textures are indicative of brecciation caused by fluidisation.

4.6. Brecciated shungite rocks

Brecciated shungite rocks are distinguished from the massive variety by joints (Fig. 4f), whereas cryptocrystallinity is retained and the principal mineralogical and chemical compositions remain unchanged (Filippov, 1994a). Four main types of brecciated shungite rocks have been recognised and are locally termed (1) jointed rocks, (2) ‘cryptic’ breccias, (3) quartz-cemented breccias and (4) marginal breccias.

The jointed rocks are black, mat and cryptocrystalline. They form lenses tens of metres thick with no preferential spatial distribution with respect to the orebody (Fig. 6, Profile C–D). One- to two-centimetre long joints form polygonal systems, a combination of concentric and radial systems, or a system of orthogonal joints. The jointed pattern observed is similar to that resulting from syneresis. Thus, these joints are considered to represent syneresis cracks

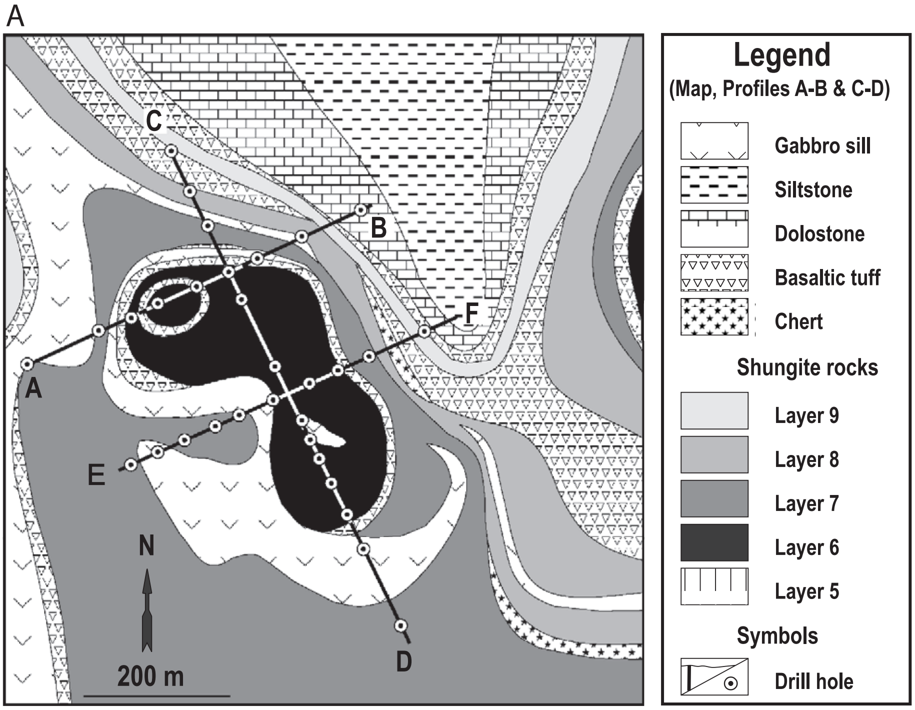

Fig. 6. Geological map of the Maksovo deposit, with cross- and longitudinal profiles through the cupola structure (modified after Kupryakov, 1994). Note that the deposit is confined to Layer 6. The thickness of shungite rocks decreases towards the margins of the cupola structure (Profiles A–B and C–D). Distribution of the C_{org} content reveals a mushroom-like structure in the centre of the ore body (Profile E–F).

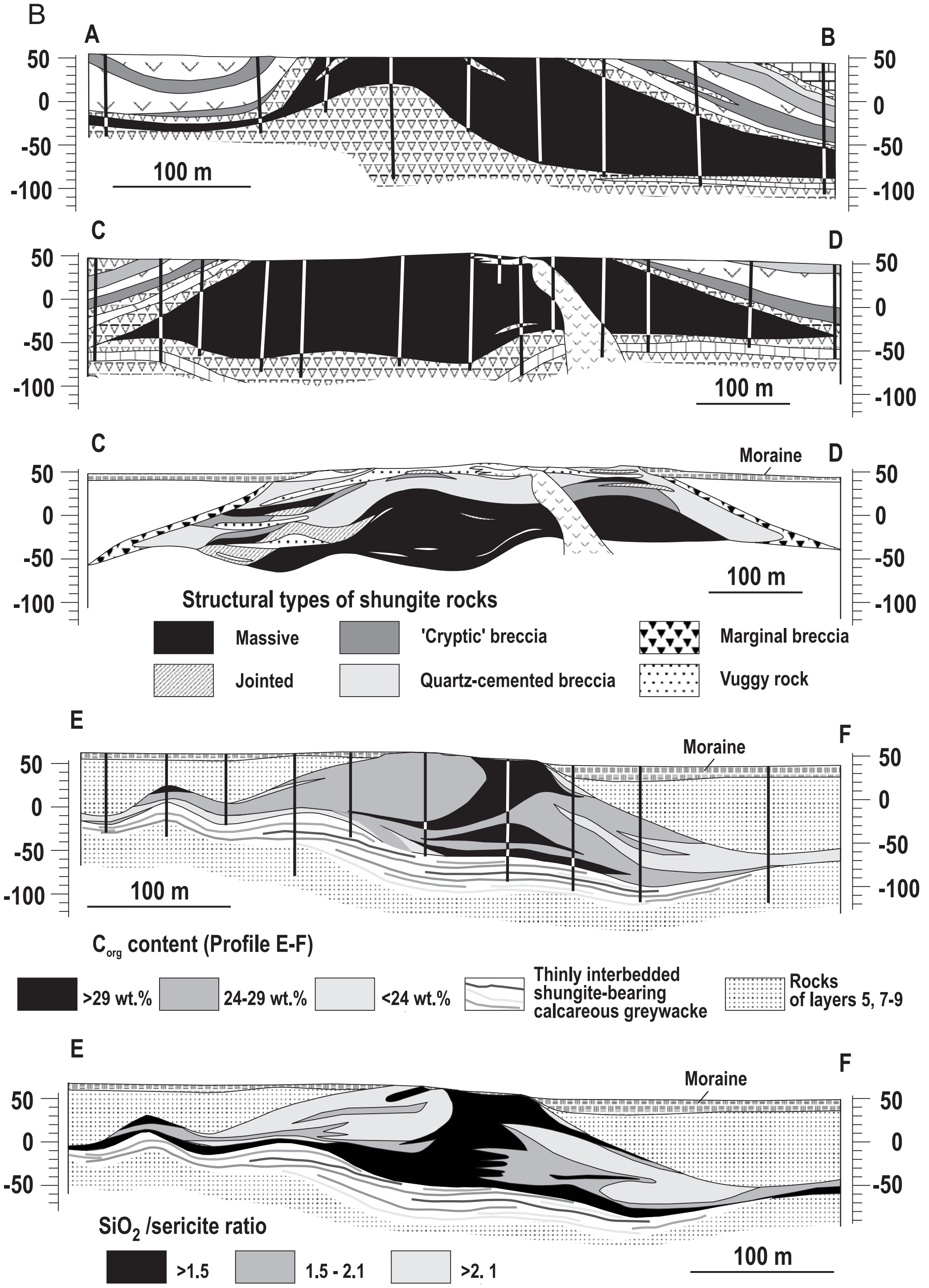

Fig. 6 (*continued*).

formed by the spontaneous expulsion of water or other liquids from the organosiliceous gel during aging. The open joints are filled with quartz (Fig. 5c) and, in some cases, thin vein-shungite and scattered pyrite crystals.

The ‘cryptic’ breccia is a black, mat rock with lustrous specks, flaser-like and fluidal structures found above the massive shungite rocks on both flanks of the orebody (Fig. 6, Profile C–D). The term ‘cryptic’ breccia is applied to the massive shungite rock with a structural pattern described as ‘cryptic structural heterogeneity’. The latter is distinguished by chaotically distributed millimetre- to centimetre-size, angular and flame-shaped, jointed, dark grey shungite fragments in a pale grey heterogeneous matrix (Fig. 5d), which is, in turn, composed of micron-size, elongated rounded, dark grey shungite fragments distributed in the pale grey shungite framework (Fig. 5e). Irregular structural organisation of large and small fragments results in the development of three main types of fabric: brecciated, flaser-like and irregular fluidal. The pale grey shungite framework exhibits well pronounced cleaved microfabrics. The cleavage crosses fluidal fabrics and elongated fragments at various angles implying that the fluidal textures were not caused by tectonic stresses and are a primary feature.

Large fragments of dark grey shungite have abundant shrinkage cavities of different shapes filled with microglobular shungite. These also show syneresis cracks. Peculiar mm-size fragments with spectacular micron-scale concentric structures are abundant locally (Fig. 5f). These rice-grain-shaped fragments always exhibit an orientation coinciding with the fluidal fabrics. The ‘cryptic’ breccia is specifically marked by syneresis cracks occurring in shungite from macro- to microscale. The overall textural development observed in the ‘cryptic’ breccia can be explained by the brecciation and fragmentation associated with multiple fluidisation processes. Abundant syneresis cracks suggest that shungite rocks formed from organosiliceous gel.

The quartz-cemented breccia occurs as a 20-m-thick ‘apron’ in the upper part of the orebody overlying massive shungite rocks as well as ‘cryptic’ breccias (Fig. 6, Profile C–D). Angular fragments ranging from 1 to 5 cm in size are cemented by quartz. The volume of quartz may reach 30% in zones of intensive brecciation that developed in an extensional, decompressional regime.

The marginal breccia develops as a 10-m-thick continuous ‘layer’ along the upper contact of the orebody (Fig. 6, Profile C–D) and incorporates fragments of both country rocks (dolomite-rich siltstone) and the shungite orebody cemented with quartz-carbonate material. All fragments exhibit *in situ* brecciation with limited rotation and tectonic modification implying that the brecciation was associated with an extensional, decompressional regime similar to that of the quartz-cemented breccia.

4.7. Vuggy shungite rock

Massive shungite rocks with ‘cryptic’ structural heterogeneity and ‘cryptic’ breccias contain abundant vugs that occur in lenses in the upper part of the orebody (Fig. 6, Profile C–D). They also occur in the inner part of the body occupying apical parts of small-scale antiformal structures. The spheroidal vugs are 3–5 mm in diameter and formed from shrinkage of larger irregular vugs that resemble gas-escape structures. The smaller vugs are filled with shungite (Fig. 5g,h), whereas the larger ones contain other material. Shungite lines walls of the vugs whereas quartz occupies their centres (Fig. 5i). Shungite filling the vugs is commonly characterised by a globular structure (Fig. 5g,h) and displays syneresis cracks implying that the organosiliceous material formed from a gel.

4.8. Vein-shungite

The latest generation of mobilised and migrated shungite is represented by the vein-shungite that forms sub-vertical veinlets up to 15 cm thick (Fig. 4g). The veinlets develop in an open extensional fault with well-defined, planar walls that can be traced over a distance of ca. 20 m. The vein-shungite is lustrous and extremely brittle with all joints filled with jarosite.

4.9. C_{org} distribution

Distribution of C_{org} within the orebody shows very peculiar patterns. In some sections, it simply emphasises the cupola-like geometry of the orebody (Fig. 6, Profile E–F), whereas in others the C_{org}-rich rocks appear in the form of a mushroom-shaped body as well as in the form of cupolas located in apical parts of small antiformal structures (Fig. 6, Profile E–F). The spatial distribution of the quartz/sericite ratio displays somewhat more complex patterns. The lowest ratios are associated with rocks enriched in C_{org} as well as with those in the footwall of the orebody (Fig. 6, Profile E–F).

4.10. Clastic shungite deposits

A deposit of clastic shungite that has been mined since 1972, occurs in the Kondopozhskaya Formation near Nigozero (Figs. 1 and 2). The Nigozero deposit is a ca. 500-m-thick unit that lies unconformably on basalts of the Suisarskaya Formation (Fig. 7). The rocks of commercial interest are low shungite siltstones with total reserves of 36 million tonnes with additionally prospected reserves in the adjacent area exceeding 450 million tonnes. One quarry has an annual production of 600,000 tonnes of rock, which is used for the manufacture of shungisite (see below).

The productive formation is a ca. 80-m-thick lens, which wedges out completely towards the southeast over a distance of 6 km (Fig. 7). The lens is mainly composed of rhythmically bedded sandstones, siltstones and mudstones. The sandstones consist of volcanoclastic material derived from underlying volcanic rocks. Among the clasts are well sorted, poorly rounded particles of basalt and andesite in a feldspar-chlorite matrix. The siltstones consist of poorly rounded grains of feldspar and quartz cemented with chlorite. Chlorite and sericite are the main constituents of the mudstones, which contain around 1 wt.% C_{org} (Table 1) in the form of shungite.

The rhythmic beds observed in the productive formation are from 2 to 15 cm thick and exhibit a sequence of sedimentary structures typical of in turbidity current deposits. Many beds start with a thin unit of massive or graded sandstone, which is overlain progressively by a fine-grained, parallel-laminated siltstone and is capped by laminated silty mudstone. These correspond to the A, B and D units of a typical Bouma cycle. Small-scale slump structures and loading features are present and desiccation cracks have been reported (Gorlov, 1984). The limited thickness of the Bouma sequences, the irregular appearance of the current-bedded C unit, and fine clast size suggest that the sediments were deposited

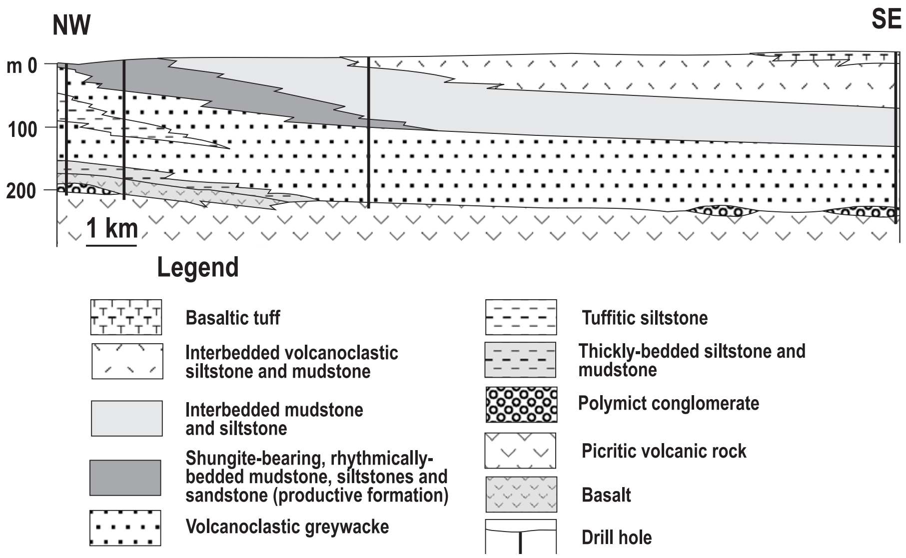

Fig. 7. The Nigozero deposit of the low shungite rocks. The drilled profile shows that the productive lens wedges out rapidly southeastwards (modified from Gorlov, 1984).

from a multiple turbidity current pulse in a distal part of the basin. The absence of sulphides and thin plane-parallel lamination of the background sedimentary rocks are consistent with the lacustrine origin of the basin.

Two stratigraphic levels in the productive formation are marked by the presence of clastic shungite. The clasts are lustrous shungite (anthraxolite) ranging in size from 0.1 to 20 cm. The clasts occurring in laminated sandstones are disc-like bodies (Fig. 4h), whereas those hosted by mass-flow-deposited breccias exhibit spheroidal forms (Fig. 4i). All anthraxolite clasts contain shrinkage cracks filled with quartz.

5. The nature of shungite rocks and shungite

5.1. Depositional environment

Rocks underlying the shungite-bearing sequence were deposited under shallow-water, evaporitic conditions in a mixed non-marine and carbonate shelf environments (Melezhik et al., 2000). The basal sediments of the shungite-bearing sequence were deposited on a surface showing evidence of an extended period of subaerial exposure. The basal part of the shungite-bearing sequence is composed of finely laminated grey siltstones (Galdobina, 1987). In places, the basal sediments are red and variegated, thinly laminated siltstones and are of lacustrine rather than marine origin (Melezhik et al., 2000). Melezhik et al. (1999) suggested that the shungite-bearing sequence was accumulated on in the rift-related basin, which formed at ca. 2.0 Ga ago on a rifted margin of the Karelian craton, apparently during the development of the Svecofennian Ocean. Alkaline affinities, considerable thickness and aerial distribution of coeval basaltic volcanism provide evidence that the rift-bound basin experienced flooding of basaltic magma erupted on to the submerged continental crust (Pukhtel et al., 1998).

The integrated sedimentological, geochemical and isotopic data suggest that initial accumulation of organic-rich sediments took place in brackish, sulphate-poor water within a non-euxinic lagoon (Melezhik et al., 1999). Basalts, tuffs and tuffites in the succession reflect the influence of synchronous basaltic volcanism (e.g., Galdobina, 1987) and contemporaneous submarine hydrothermal activity led to abundant chert.

5.2. The genesis of syngenetic shungite deposits

The unusual accumulation of C_{org} in the Onega area was likely the result of (1) a high level of biological productivity and (2) a high degree of preservation of biologically produced material. It is most likely that extensive explosive volcanism delivered both nutrients, thus increasing both production of organic matter and its subsequent preservation (Melezhik et al., 1999). Sedimentological and isotopic data (Melezhik et al., 1999) have confirmed a biological origin of shungite (Rankama, 1948; Chukhrov et al., 1984) and suggest that organic matter experienced various post-depositional alterations and generation of petroleum.

Shungite rocks from in situ stratified deposits, containing less than 50 wt.% of dispersed shungite commonly retain sedimentary structures and can be identified as metamorphosed oil-shales. Those shungite rocks containing more than 50 wt.% C do not show primary sedimentary bedding and lamination, which has been explained as due to the contribution of allochthonous organic matter and migrated bitumen causing the rocks to lose their primary sedimentary lamination (Melezhik et al., 1999). In addition to autochthonous kerogen residue, semilustrous and semimat shungite rocks contain allochthonous organic matter, i.e., migrated petroleum.

The diapir shungite deposits commonly do not exhibit sedimentary layering except where C_{org} content is <20 wt.%. As they are composed of cryptocrystalline silica and C_{org} and form a mushroom-shaped body (Fig. 6), these rocks likely formed from organosiliceous gels or mud. Cryptic breccias contain peculiar fragments with micron-scale concentric structures (Fig. 5f), which might have formed by a self-organising mechanism. A very gentle, delicate erosion of one concentric pattern by another (Fig. 5j) suggests formation by a reaction between two chemically different hydrocarbon liquids.

Based on studies of Phanerozoic oil fields (Hedberg, 1974; Gretener, 1969), we suggest that the organosiliceous rocks developed at Maksosvo represent relict diapir structures or remnants of mud volcanoes. The recent discovery of this type of shungite rocks (Fig. 8) by exploration geophysics supported by drilling suggests a wide aerial distribution.

5.3. Genesis of migrated shungite

Migrated forms of shungite in the form of vein- and layer-shungite, as well as shungite filling vugs and cementing breccias, represent metamorphosed bitumen, formed from petroleum (Melezhik et al., 1999). Textures of shungite observed in the rocks suggest that there were several episodes of generation and migration of petroleum. Shungite-filled vesicles in subaerially erupted basalts indicate that the earliest phase of oil generation took place

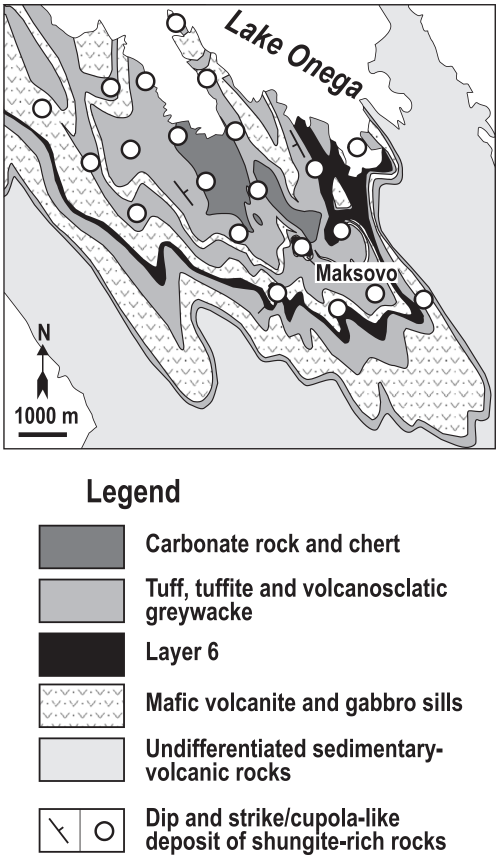

Fig. 8. Simplified geological map of the Tolvuya synform showing the position of the Maksovo shungite deposit. White circles indicate positions of new occurrences and deposits of shungite (organosiliceous) rocks appearing in the form of cupola-like bodies.

prior to burial. Assuming a maximum sediment thickness near ca. 500 m, it is unlikely that in the early stage of basin development a normal burial could have provides the temperature required for oil generation. The most likely heat source for the earliest maturation of hydrocarbons would be the coeval volcanism.

Isotopic data suggest that the main source of liquid hydrocarbons was apparently located within the lower part of the upper Zaonezhskaya Formation (Melezhik et al., 1999). However, the main sources of shungite-rich rocks containing >50 wt.% C_{org} are confined to small-scale, cupola-like structures. Shungite-rich rocks are intensively brecciated thus indicating that allochthonous organosiliceous material was emplaced prior to a major phase of deformation. The brecciation resulted in the generation of close spaced open joints. However, it is not yet clear whether the brecciation was related to the development of diapir-like structures, was associated with the development of mud volcanoes, or was caused by the extensional tectonic regime. However, it is possible that the sub-horizontally plunging synforms and antiforms structures in the area (Fig. 1) were originally generated by horst-and-graben structure formed during rift inversion.

This implies that prolific amounts of liquid hydrocarbon, the remnants of which have since solidified, were generated through the 'oil window' opened during burial of the shungite-bearing sequence prior to the rift inversion. This also suggests that vertical and lateral migration of liquid hydrocarbon and perhaps undifferentiated organosiliceous gels or mud towards the antiformal and interbedded traps was coeval with the early stage of the rift inversion, whereas the advanced stage resulted in partial loss and/or oxidation and solidification of liquid hydrocarbon and dewatering of organosiliceous gels. The oxidised hydrocarbons became solid bitumen that was subsequently joined. Massive organosiliceous rocks in the Maksosvo and other similar deposit as well as the semilustrous, semimat shungite rocks and vein-shungite at Shunga apparently were emplaced during the early stage of rift inversion. Vein-shungite as well as shungite-quartz low-temperature hydrothermal paragenesis filling vugs and cementing joints and fragments in breccias are apparently related to the metamorphic stage.

5.4. Genesis of clastic shungite

The deposits containing clastic lustrous shungite are separated from the stratified and diapir shungite deposits by a 500-m-thick formation of mafic lava and volcanoclastic greywacke (Fig. 2). The clastic shungite (Fig. 4h,k) probably represents redeposited bitumens. Oil leakage was likely caused by extensional tectonics that fractured oil reservoirs in the underlying sequence that contains most shungite.

6. Microstructural organisation of shungite

Microstructurally, shungite is a very complex material (Khavari-Khoransani and Murchison, 1979; Buseck and Huang, 1985; Jehlicka and Rouzaud, 1993; Kovalevski et al., 1994; Yushkin, 1994). High-resolution transmission electron microscopy (HRTEM) suggests that in some cases shungite carbon occurs in the form of nanometre-scale globular structures (Fig. 5k,l, Kovalevski et al., 1994). Although a consensus of opinion on microstructural configuration of shungite carbon has not yet been reached, one working hypothesis is that shungite likely represents a new structural form of carbon, which has not been previously described from natural environments (Kovalevski and Melezhik, 2000). It seems that carbon may occur in the form of globular structures analogous to fullerenes but measuring about 10 nm across (Yushkin, 1994; Kovalevski et al., 1994).

However, Khavari-Khoransani and Murchison (1979), Yushkin (1994) and Golubev (2000) suggested that shungite carbon represents mesophasic organic matter with heterogeneous molecular structure in which two structural elements can be distinguished. Buseck and Huang (1985) demonstrated that some shungite grains are characterised by parallel sets of fringes showing some structural order. Although layers are short and contorted, the edges of some grains show long and relatively uniformly spaced fringes approaching those of graphite. The second structural element was observed in the grain interior, which exhibits either a low degree of structural organisation with contorted irregular fringes or no organisation at all. These structurally disordered interiors may occupy a large volume of shungite (i.e., >50 wt.%, Berezkin et al., 2000). There are also areas, tens of nanometres across, within shungite material that show no structure, even when imaged using HRTEM. However, it is not known whether bonds exist between C, H, N and O in this non-crystallised shungite. Surprisingly, the microstructural properties of shungite remain unchanged and are not graphitised by heating, even at 2900 °C (Khavari-Khoransani and Murchison, 1979).

7. Practical applications of shungite and shungite rocks

Shungite has been known in Karelia since the middle of the 18th century when weathered shungite rocks were first used as a base for making black paints. In the 1800s slates and dimensional stones extracted from small quarries in the Onega area were used for buildings and decorations of the Cathedral of the Kazan Icon of the Virgin, the Isaac Cathedral, the Winter Palace and the Russian Museum in St. Petersburg. A serious shortage of fossil fuel at the end of the 19th century and, later, from 1914 to 1917 and from 1930 to 1932 caused several intensive but unsuccessful technological tests to be made for using shungite as a coal substitute.

The practical use of shungite rocks as an industrial mineral began in the 1970s when low shungite rocks (0.1–2.0 wt.% C_{org}) were widely used for the production of a markedly expanding, highly effective insulation material. Aggregates of low shungite rocks from the Nigozero deposit heated at 1090–1130 °C show remarkable expansion and convert into globular particles with a specific gravity less than 0.25–0.50 g/cm^3. The expanded material has been termed shungisite and is used as a light filler in concrete constructions. Mass production of shungisite has been developed as a substitute for keramsite.

Systematic investigations of chemical and physical properties of shungite performed in the 1970s and 1980s have led to other uses (e.g., Sokolov and Kalinin, 1975; Sokolov et al., 1984; Kalinin, 1984). Shungite has exceptionally high resistance in chemically aggressive environments and has a high electrical and low thermal conductivity (e.g., Rozhkova, 1994). Shungite is characterised by low specific gravity (1.8 g/cm^3) and unusually high specific surface areas (up to 500 m^2/g, Table 2, Sokolov et al., 1984) comparable to that of activated carbon (450 and 1000 m^2/g) (Kinoshita, 1988).

Other uses include: (i) electrothermal production of ferroalloys, P, Cu, Ni and Co; (ii) a coke and flux substitute for ferrosilicium, silicomanganese and cast iron production; (iii) a filler in acid-resistant and refractory materials; (iv) a graphite substitute in flame-resistant paints and pastes; (v) electrically conductive fillers to protect against electromagnetic radiation across a large frequency range.

Additionally, shungite and shungite rocks have a wide range of practical use in environmental applications. Shungite can absorb various organic and inorganic substances, pathogenic bacteria and heavy metals from paper industry waste waters (Dyukkiev et al., 1992). Waste waters from oil-processing plants are more efficiently purified by shungite sorbents than by chlorine, coagulants, or electrochemical treatment methods. Shungite filters extract phosphorus and disinfect sewer waters after biological purification. Electrochemical studies of shungite have revealed a unique anode behaviour of shungite carbon in lidites (1–4 wt.% C and 95 wt.% SiO_2), resulting in the formation of oxides, which are resistant in acids under positive potentials. This has no analogue among carbonaceous materials although the results are comparable to the anodic oxidation of gallium arsenate (Zaidenberg et al., 1991).

Table 2
Physical characteristics of shungite and shungite-bearing rocks

Composition/property	Layer- and vein-shungite	shungite-bearing rock			
Average C, %	98	60	30	14	3
Specific gravity, g/cm^3	1.83	2.0	2.13	2.7	2
Maximal specific surface area, m^2/g	500	10	20	6	2.6
Effective pore radius, Å	20–40	40–60	30–60	–	–
Heat conductivity, W/(m × °C)	2.2–3.6	2.5–3.5	5.2	3.8–5.4	8.2
Elastic modulus, $E \times 10^{-5}$ MPa	0.19–0.24	0.26–0.31	0.31	0.51	0.83

All the practical applications listed above have been developed at different levels ranging from laboratory experiments and to the industrial scale (e.g., Sokolov et al., 1984; Bel'skaya et al., 1985) and rely on shungite-bearing rocks containing >20 wt.% carbon.

8. New practical applications, cheap fullerenes: myth or reality?

The discovery of the geological occurrence of fullerene in Karelian shungite (Buseck et al., 1992) led to further investigations of the molecular structure of shungite. Fullerenes or buckyballs, are a creature of the laboratory (Amato, 1992). The great demand for fullerenes (mostly due to their superconductivity) and high production costs has resulted in high prices. In the early 1990s, commercial sources offered purified fullerenes at retail prices of US$2800 and US$10,700 per gram for C_{60} and C_{70}, respectively. By 1993, C_{60} and C_{70} fullerenes manufactured in the United States sold at retail prices of US$150–350 and US$1250–3500 per gram, respectively, and by 1994 prices had fallen to US$100–250 and US$600–3000 per gram, respectively (Lane, 1994). Although prices have diminished over time, the cost of artificially produced fullerenes on the market remains high, comparable with prices for gold. Discovery of fullerenes in geological environments may have serious consequences on prices. Additionally, and perhaps more importantly, fullerenes formed in a low-temperature, greenschist facies ($\approx$ 350 °C) natural environment may allow more efficient, low-cost production of fullerene.

Trace concentrations of fullerenes (C_{60} and C_{70}) in shungite from the Shungskoe deposit were first discovered by means of a HRTEM and confirmed by Fourier transform mass spectrometry (Buseck et al., 1992). Later fullerenes were extracted from shungite-bearing rocks, and concentrations were estimated to be as high as 0.1 wt.% (Holodkevich et al., 1993).

Subsequently, efforts by some other investigators to confirm the discovery in Karelian shungite were unsuccessful (Yushkin, 1994; Ebbesen et al., 1995; Vinokurov et al., 1997; Buseck, 2002; Mossman et al., 2003). Yet, other studies corroborated the presence of trace amounts (0.1–10 ppm) of fullerenes (Masterov et al., 1994; Parthasarathy et al., 1998; Rozhkova and

Andrievsky, 2000), and Reznikov et al. (1998) even estimated the fullerenes content to be 0.5–1.0 wt.% with a probable content up to 3–5 wt.%. Based on these publications, inferred reserves of fullerenes in the Onega area were estimated at 1–3 million tonnes (Polekhovsky and Reznikov, 1999; Reznikov and Polekhovsky, 2000).

At present, it is still unclear whether the reported natural fullerenes are (i) present in very low concentrations, (ii) not recoverable using techniques tried to date, (iii) present in larger amounts, but only in selected parts of the deposit, and (iv) artefacts of the sample preparation technique. We are not in a position to consider objectively these options at the moment and leave this exercise for future research. However, the fourth possibility warrants further discussion, i.e., whether fullerenes may form in variable amounts during analyses depending on the methods used. As stated above, accurate knowledge regarding the chemical bonds of poorly crystallised varieties of shungite is not available. A partial depolymerisation suggests that when structurally disordered shungite carbon is subjected to heating at 380 °C under a hydrogen pressure of 22–35 MPa extraction of diphenyl and its derivatives-aromatic compounds with isolated benzene nucleus takes place (Bondar et al., 1987). As the diphenyl was theoretically considered as a structural element from which fullerenes could be synthesised (Lemanov et al., 1994; Eletsky and Smirnov, 1995), shungites may be an appropriate raw material for synthesis of fullerenes.

9. Conclusions

Discovered in 1789, shungite is a black, non-crystalline, non-graphitised, structurally heterogeneous, glassy mineraloid with a semi-metallic lustre containing >98 wt.% C. Around 25×10^{10} tonnes of shungite occur mainly in the dispersed form in a 2.0-Ga 1000-m-thick sedimentary-volcanic succession developed over an area of 9000 km^2 on the northern shore of Lake Onega, NW Russia.

The occurrences of shungite and shungite-bearing rocks near Onega Lake represent a rare case of a petrified oil fields, diapirs and oil seeps. Major shungite deposits occur either in the form of stratified shungite-rich rocks or as diapirs. The former represent metamorphosed oil-shales and migrated bitumen, originally liquid hydrocarbons, whereas the latter represent organosiliceous rocks (35–75 wt.% SiO_2 and 20–55 wt.% C_{org}), formed from gels or mud. The genesis of organosiliceous rocks forming the diapirs raises certain problems but origins as diapirs or mud volcanoes origin or a combination of both seem likely.

Shungite is represented by mesophasic organic matter with heterogeneous molecular structure where carbon occurs in the form of 10 nm globules irregularly distributed within carbon showing no structure. Shungite is characterised by a low specific gravity (1.8 g/cm^3), unusually high specific surface areas (up to 500 m^2/g) and exceptionally resistance in aggressive environments. Shungite has a high electrical and a low thermal conductivity. Shungite can serve as a active reducing agent, a catalyst and a sorbent. The unusual properties of shungite are used in diverse industrial and environmental applications including metal production, metallurgy, water purification, high-technology uses, thermolysis and organosynthesis of cyclic hydrocarbons. Shungite also is an effective sorbent for removal of organic and inorganic substances, pathogenic bacteria and heavy metals from solutions.

Several articles have reported the presence of fullerenes in shungite but its presence in shungite has not been firmly established. Despite this uncertainty, it seems likely that shungite may be used as a raw material for the synthesis of fullerenes.

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