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SHUNGITES: THE C-RICH ROCKS OF KARELIA, RUSSIA

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ABSTRACT

The Lower Proterozoic rocks (2.0 to 2.1 Ga) of the Shunga district near Lake Onega, Karelia, Russia contain large amounts of elemental carbon – about 25×10^{10} tonnes in an area of roughly 9,000 square kilometers. The rocks occur in a horst–graben transition zone between the Baltic Shield and the Russian Platform. Biogenic, metasomatic, and volcanogenic origins have variously been proposed for the carbon in these rocks. Most rocks in a 1200- to 2000-m stratigraphic sequence contain at least several weight percent carbon, and localized areas contain up to 98 wt% glassy carbon, a most unusual natural form. The glassy carbon is deep black, has a pronounced conchoidal fracture, and a Mohs hardness of 3.5. Its high luster makes it look almost metallic; it has a low density (1.9–2.0 g/cm^3) and high electrical conductivity (about 100 S/cm). The glassy bodies are relatively small (tens of meters in extent) and extremely brittle. The carbon shows diffuse X-ray spectra; high-resolution transmission electron microscopy images indicate that limited structure exists, primarily in the form of poorly organized graphite-like layers in roughly rounded units, but there is considerable heterogeneity. Analysis of carbon isotope ratios of samples from three localities yields $\delta^{13}C$ values between –26.4 and –37.6‰ PDB. Values correlate to locality rather than to rock type, suggesting that the glassy carbon was locally remobilized from the surrounding country rocks. In one sample, clasts of almost pure glassy carbon have a value of –37.5‰ and occur in a matrix containing roughly 30 wt% carbon with a composition of –37.6‰. In samples from another locality, vein material of almost pure carbon (–26.7‰) cross-cuts rock of the same isotopic composition (–26.5‰), but also with only roughly 30 wt% carbon. The authors differ regarding the implications of the carbon-isotopic data. JWV and PRB interpret them as indicating a biogenic origin, either *in situ* or remobilized during low-grade metamorphism, whereas LPG interprets the field and isotopic data as indicating an abiogenic, volcanic origin.

Keywords: shungite, glassy carbon, Proterozoic, carbon isotopes, Shunga, Karelia, Lake Onega, Russia.

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Sommaire

Les roches d'âge protérozoïque inférieur (de 2.0 à 2.1 Ga) du district de Shunga, près du lac Onega, Karélie, en Russie, contiennent des quantités importantes de carbone à l'état élémental, environ 25 × 10[10] tonnes dans une région d'environ 9,000 kilomètres carrés. Les roches se trouvent dans une zone de transition avec horsts et grabens entre le bouclier baltique et la plate-forme russe. Des processus biogénique, métasomatique, et volcanogénique ont été proposés pour expliquer la formation du carbone dans ces roches. La plupart des roches dans une séquence stratigraphique de 1200 à 2000 m contiennent au moins quelques pour cents (poids) de carbone, et à certains endroits, il y a jusqu'à 98% de carbone à éclat vitreux, aspect très rare. Il s'agit d'un matériau noir foncé, ayant un cassure conchoïdale, et une dureté de Mohs de 3.5. Son éclat frappant fait presque penser qu'il s'agit d'un métal. Ce matériau, appelé couramment shungite, a une faible densité (1.9–2.0) et une conductivité électrique élevée (environ 100 S/cm). Les masses à aspect vitreux sont de dimensions assez restreintes (dizaines de mètres) et très cassantes. Le carbone montre un spectre flou en diffraction X; en microscopie électronique à transmission à résolution élevée, il semble y avoir une structure cristalline sur une échelle locale, surtout sous forme de domaines de graphite imparfaitement agencés plus ou moins arrondis, mais avec une hétérogénéité assez importante. Une analyse des rapports isotopiques du carbone provenant d'échantillons de trois endroits a donné des valeurs de $\delta^{13}C$ entre –26.4 et –37.6‰ par rapport à l'étalon PDB. Ces valeurs montrent une corrélation avec le site de prélèvement plutôt qu'avec le type de roche, ce qui fait penser que le carbone "vitreux" a été remobilisé localement à partir des roches encaissantes. Dans un échantillon, des fragments de carbone presque pur donnent une valeur –37.5‰, et se trouvent dans une matrice contenant environ 30% de carbone par poids ayant une composition isotopique de –37.6‰. Dans un autre endroit, un échantillon de carbone presque pur prélevé d'une veine (–26.7‰) recoupe une roche hôte dont le carbone a sensiblement la même composition isotopique (–26.5‰), quoique la teneur en carbone est seulement environ 30%. Nous ne présentons pas une interprétation unanime de ces données isotopiques. Selon JWV et PRB, il s'agirait de carbone d'origine biogénique, soit *in situ* ou bien remobilisé au cours d'une recristallisation métamorphique de faible intensité. Selon LPG, les observations de terrain et les données isotopiques indiqueraient plutôt une origine abiogénique, voire volcanique.

(Traduit par la Rédaction)

Mots-clés: shungite, carbone "vitreux", protérozoïque, isotopes de carbone, Shunga, Karélie, lac Onega, Russie.

Introduction

The rocks of the Shunga district in the northwestern region of Lake Onega, Karelia in Russia have long attracted interest because of their abundant carbon. It occurs throughout much of the Lower Proterozoic sequence, with contents locally ranging up to 98 wt% and consisting of almost pure glassy carbon. The carbon-bearing rocks are in an area of approximately 9,000 square kilometers that contains about 25 × 10[10] tonnes of elemental carbon (Galdobina 1993).

In addition to their geological interest, the carbon-rich rocks of the Shunga region have properties that make them useful to industry. For example, by heating in air between 1080 and 1100°C, samples containing only 1 wt% carbon have been converted to highly porous, pumice-like rocks that have been used commercially for insulating fillers (Sokolov & Kalinin 1975). Samples containing 25 to 35 wt% carbon have been added to concrete to make it an electrical conductor, resulting in a product that is useful for resistive heating as well as providing shielding against electromagnetic radiation in a frequency range of more than 10 MHz at a level of not less than 100 dB (Solovov *et al.* 1990). Addition of powdered rocks to plastics and rubber improves their mechanical properties, particularly their thermal expansion and resistance, and high-frequency conductivity. Shungite rocks have been mined for their use as antifriction agents when placed into composites; they are also effective sorbents for removal of both organic and inorganic substances from water (Sokolov *et al.* 1984).

There is an extensive literature, most of which is in Russian, about the carbon-rich rocks of the Shunga region. Inostrantsev (1879) called them "shungite"; he concluded that shungite is an extreme sample of noncrystalline carbon (following the prevailing literature on shungite, we here use "carbon" to refer to elemental or organic carbon, as opposed to that present in carbonate). Despite the strong opinions of many of the people who have studied the area, there is no consensus in the literature regarding the origin of these intriguing carbon deposits. Many hypotheses have been advanced; these include biogenic (Borisov 1956, Volkova & Bogdanova 1986), metasomatic (Ivankin *et al.* 1987, Kalinin 1990, Lobzova & Galdobina 1987, Galdobina *et al.* 1995), metamorphic (Timofeyev 1924), and volcanogenic modes of origin (Fersman 1922, Artamonov & Kekkonen 1935, Sokolov & Kalinin 1975, Golubev & Akhmedov 1995). Generalov (1995) studied the opaque minerals in shungites, and suggested that these rocks have a similar origin to deposits in black shales, such as those of the Kola Peninsula. Khavari-Khorasani & Murchison (1979) and Volkova & Bogdanova (1986) proposed that the two types of shungite richest in carbon (types I and II) are meta-anthracite coal of biological origin. Although only mentioned in passing, it appears to be accepted by some petroleum geologists that shungite (of unspecified type, but presumably type I) is a highly evolved bitumen (Cornelius 1987, Meyerhoff & Meyer 1987, Meyer & De Witt 1990, Parnell *et al.* 1994).

FIG. 1. Location map for the greater Shunga region. The circled cross north of Petrozavodsk marks the position of the Shunga deposits.

In this paper, we summarize some of the salient features as well as report on the general geological setting of shungite. An added feature of interest is that the first report of the natural occurrence of fullerenes was from type-I shungite rocks (Buseck *et al.* 1992), similar to those described below.

TYPES OF SHUNGITE AND THEIR AGE

The literature is confusing as to the meaning of the term *shungite*. It has been used to describe all carbon-bearing rocks of the extensive Lake Onega region (Fig. 1), with the different types of shungite distinguished by their carbon contents. The term has also been used to describe the structural state of their carbon (Kovalevski 1994), so that shungite has been applied to both the rocks and their elemental carbon.

Some authors use shungite as an adjective, as in "shungite slate" and "shungite diabase" (*e.g.*, Sudovikov 1937), whereas others refer to shungite rocks and then specify types (*e.g.*, Sokolov *et al.* 1984). A third procedure is to use both terms, *e.g.*, "lydite (type-V shungite)" (*e.g.*, Sokolov & Kalinin 1975). Galdobina (1993) referred to "shungite-bearing" followed by the rock description (carbon content and petrography), so that in this case shungite appears to refer to the carbon within the rock (Kalinin 1990, Parfen'yeva *et al.* 1994, Zaidenberg *et al.* 1995).

For consistency with what appears to be prevailing usage, we will continue to use the term *shungite* to designate reduced-carbon-bearing rocks from the Lake Onega region. Following the terminology of Borisov (1956), they are grouped into various types on the basis of their carbon contents (Table 1). Types III to V are more abundant and widespread than types I and II.

We know of no direct measurements of the ages of the shungite rocks. They mainly belong to the Ludicovian series (Fig. 2), and all age estimates are relative to the underlying Yatulian (also spelled Jatulian) and overlying Suisarian rocks. The U–Pb ages of zircon in the carbonates and diabase of the upper Yatulian horizon are, respectively, 2.15 and 2.30 Ga (Levchenkov *et al.* 1990). Sm–Nd measurements of Suisarian picrite basalts indicate an age of 1.98 Ga (Puhtel *et al.* 1992), which coincides well with the Lower Proterozoic stratigraphy of the Baltic Shield (Levchenkov *et al.* 1990). From these data, we estimate the age of the shungite rocks as between 2.0 and 2.1 Ga. On the basis of its widely disseminated, fine-grained nature and field relations, Galdobina (1987) assumed that the carbon is endogenic and of comparable age to the host rocks.

TABLE 1. TYPES OF SHUNGITE, BASED ON CARBON CONTENT*

Types	Carbon content †	Physical appearance	Abundance	Major host-rocks
I	>75 – 98	black, glassy luster; conchoidal fracture	very low	Shungite types -II and -III
II	>35 – 75	black, slightly glassy luster; prominent rectangular jointing; layered	low	dolomite, lydite
III	>20 – 35	black, dull luster; massive	medium	limestone, dolomite, tuffite
IV	>10 – 20	black, dull luster; heavily jointed; locally friable	high	sandstone, dolomite
V	≤ 10	grayish to deep black; fine grained (~10 μm diameter); massive	high	sandstone, dolomite

* after Borisov (1956), with data of Inostrantsev (1879) and Artamonov & Kekkonen 1935). † expressed in wt.%.

GEOLOGICAL SETTING AND STRUCTURE

The Karelian shungite rocks are prominent in the area around the northwestern part of Lake Onega. Galdobina (1987, 1993) and Ivankin *et al.* (1987) have summarized the Proterozoic geology of this region (called "the Onega structure"), and the following discussion is based largely on the information given in those papers.

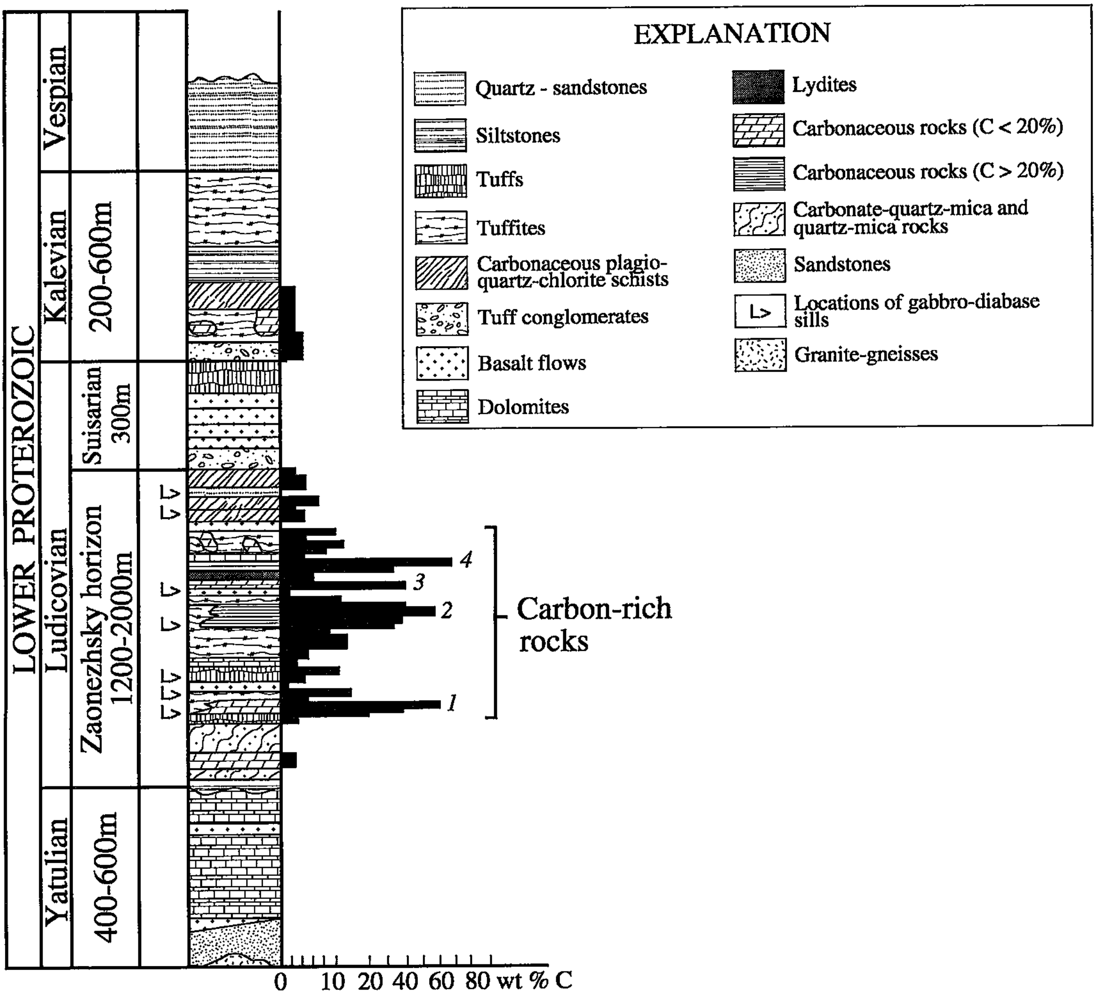

FIG. 2. Stratigraphy of rocks of the Onega structure, around the northwestern part of Lake Onega (Galdobina 1987). Carbon concentrations: 1,3 from drill holes, 2 Zaghogino and Maksovo deposits, and 4 Shunga deposit. L> indicates the location of dikes or sills.

The Onega structure is located in a formerly tectonically active transition zone between the Baltic Shield and the Russian Platform. The zone is bent in a flexure-like manner and is cut by many deep NE–SW- and shallower NW–SE-trending faults (Fig. 3). On the basis of aerial photography and confirming drill-holes, wide grabens alternate with narrow horsts.

The Onega structure is filled with Lower Proterozoic rocks (Fig. 2). From the top down they are: (a) sandstones of Vespian age, preserved in the cores of small synclinal structures, (b) 200 to 600 m of carbonaceous rocks of Kalevian age, (c) 1200 to 2000 m of carbon-bearing rocks of the Ludicovian sequence which, depending on locality, include between four and ten sills of diabase, with total thicknesses up to 1200 m, and (d) 400 to 600 m of carbonate rocks of Yatulian age. The Onega structure is surrounded by Archean rocks, mainly granite gneisses, although Upper Archean greenstones and Lower Proterozoic Sumian and Sariolian formations occur in its northwestern corner.

The Ludicovian sequence is of special interest. It consists of the Suisarian and carbon-bearing Zaonezhsky suites (Fig. 2). The bottom 180 to 200 m of the Zaonezhsky suite contains siltstones, dolomites, and carbonate – quartz – mica and quartz – mica rocks with dispersed sulfides. Carbon is rare in this bottom section. The upper Zaonezhsky suite includes tuffs, dolomite, basalt, and lydite (a compact, fine-grained, blackish variety of volcanogenic jasper); essentially

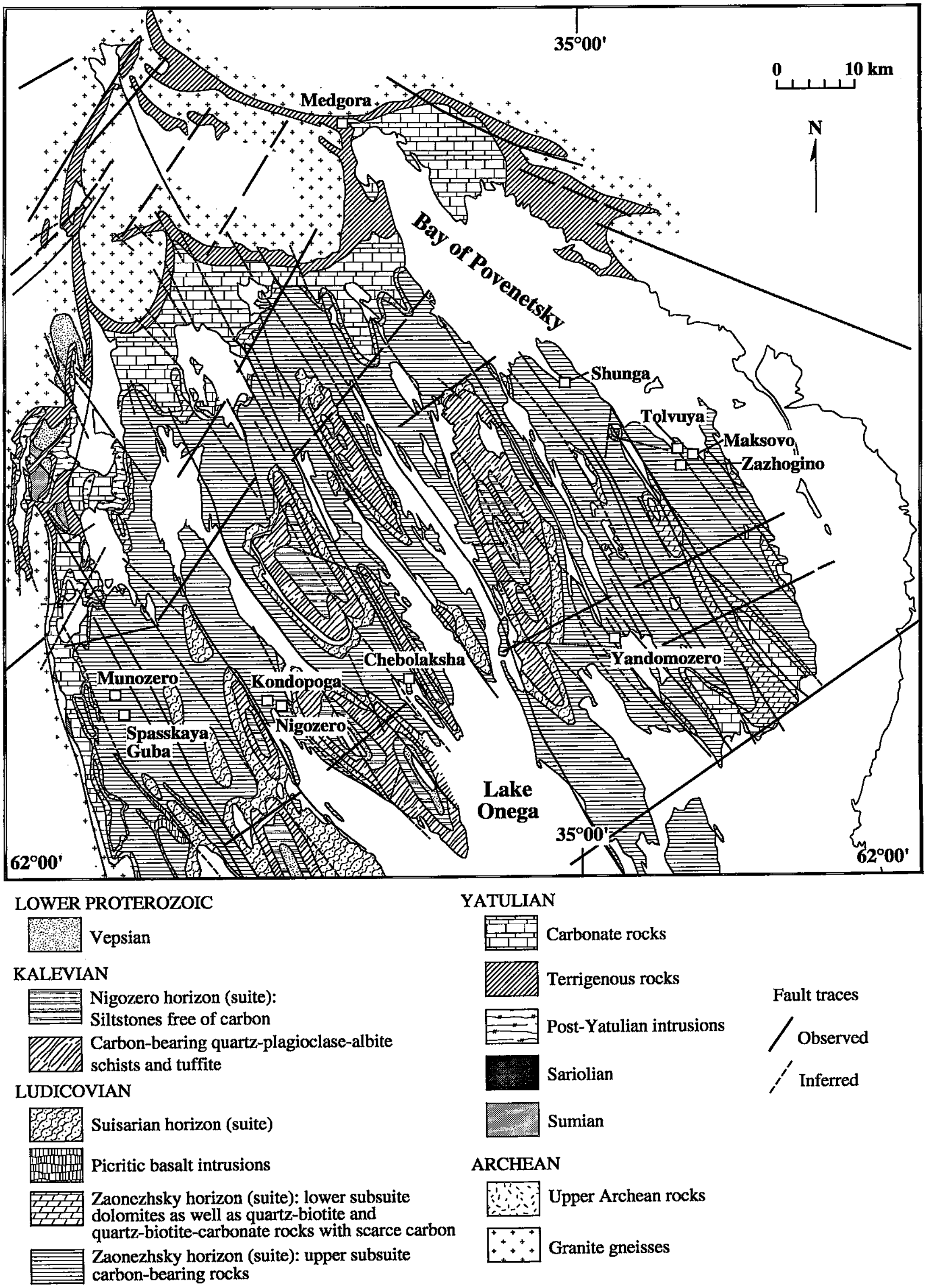

FIG. 3. Geological map of the area around the northwestern part of Lake Onega (Galdobina 1987).

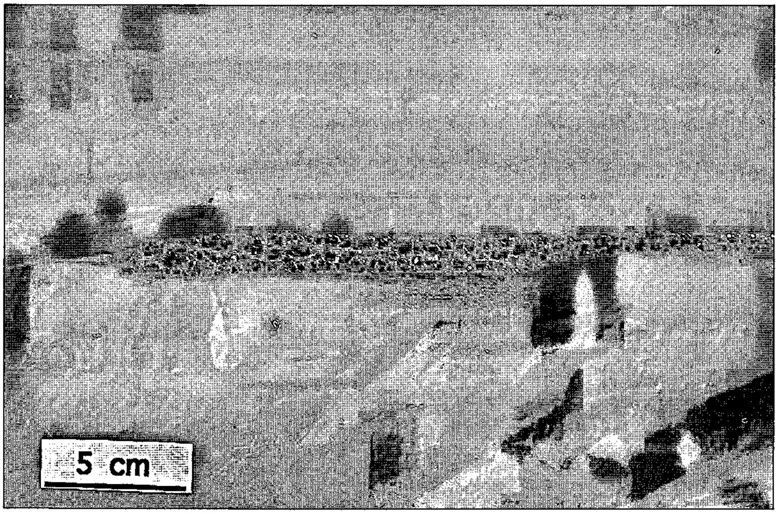

FIG. 4. Conformable lens of type-I shungite from Nigozero. The boundaries are sharp between it and the host rock, a carbonaceous plagioclase – quartz – chlorite schist.

all contain free carbon, typically 1 to 25 wt%. Late hydrothermal solutions resulted in metasomatized dolomitic rocks and sulfide ores. Diabase sills, each up to 50 to 100 m thick, were emplaced during the last stage of volcanism and appear to be associated with the carbon-bearing rocks. The degree of structural ordering of the carbon increases with proximity to the intrusions, suggesting that the carbon preceded emplacement. Pillow basalts within the sedimentary pile show that volcanism occurred during sedimentation.

The most unusual and characteristic features of the upper part of the Zaonezhsky section (600 to 650 m thick) are varied-sized bodies of carbon-rich rocks (25 to 75 wt% carbon). They occur at four stratigraphic levels (Fig. 2). In places, there are veins with carbon contents up to 98 wt%. In contrast, the Suisarian suite is essentially free of carbon and consists of basic and ultrabasic lava flows and tuffs (Fig. 2). All shungite rocks are greenschist facies (Volodichev 1987). Metasomatized dolomitic rocks lie above and below the carbon-rich horizons.

The Kalevian sequence consists of a mixture of volcanic and sedimentary rocks: tuffs, siltstones, plagioclase – quartz – chlorite schists containing up to 3 wt% carbon, and tuff-sandstones with carbon contents between 1 and 2.5 wt%. The carbonaceous rocks are up to 200 m thick, but they are absent in some cross-sections. Lenses up to 20 cm in diameter and 2 to 3 cm thick of glassy type-I shungite (Table 1) are sparse but occur locally at Nigozero within carbonaceous plagioclase – quartz – chlorite schists (Fig. 4). The Kalevian rocks are overlain by the Vespian formations.

Summarizing, the regional geology was affected by a period of continental rifting during which significant amounts of diabase dikes and sills were emplaced into a shelf sequence of strata. Tuffs and flows of basalt were interlayered with shallow marine sediments. The igneous activity provided a major source of heat that was presumably adequate for shungite formation, in addition to providing metasomatic fluids during rifting and associated magmatism.

PHYSICAL CHARACTERISTICS OF THE CARBON AND CARBON-RICH ROCKS

The rocks that are richest in carbon (type-I shungite) have a striking macroscopic appearance. They are deep black, almost glassy, with a pronounced conchoidal fracture (Fig. 5a). Their high luster makes them look almost metallic; they have a relatively low specific gravity (1.9–2.0 g/cm^3), high electric conductivity (about 100 S/cm), and some types have unusually high specific surface areas (200 to 400 m^2/g), as measured by the (BET) adsorption of gaseous nitrogen (Sokolov *et al.* 1984, Kovalevski *et al.* 1994, Zaidenberg *et al.* 1996). For comparison, commercial graphite powders have specific surface areas of approximately 10 m^2/g (Kinoshita 1988), whereas activated carbons are in the range of 450 to >1000 m^2/g (Kinoshita 1988, Parra *et al.* 1995). The brittleness of type-I shungite makes it difficult to extract pieces larger than a few cm in diameter from outcrops.

Although other natural carbon-rich species such as albertite, gilsonite, uintahite, and wurzilite can also display a conchoidal fracture, none have the semimetallic

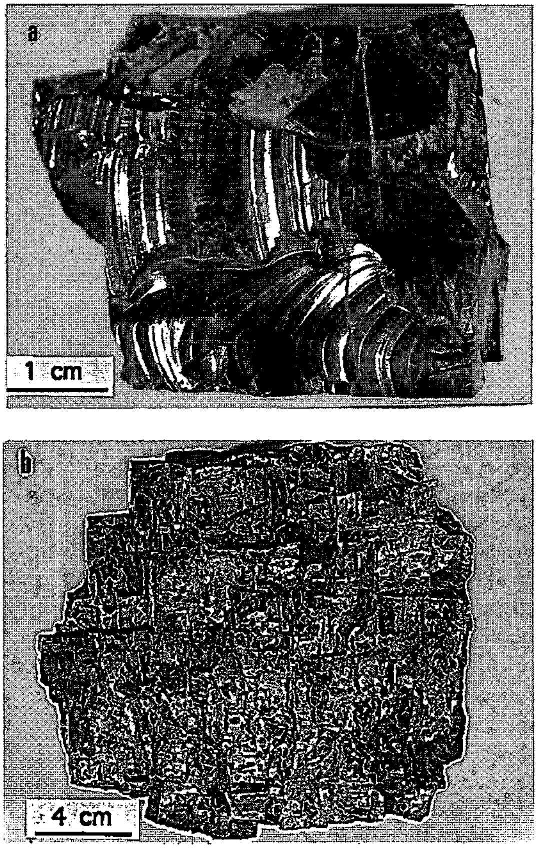

FIG. 5. Macroscopic view of hand specimens of (a) type-I shungite, and (b) type-II shungite from the Shunga mine opening. The prominent cleat-like joints are coated with jarosite (whitish color).

to metallic luster of shungite; most appear far more like hardened paving asphalt than like the shungite. High-rank anthracite is the closest in appearance, but it still appears distinctly less glassy and metallic.

Khavari-Khorasani & Murchison (1979) used optical microscopy, X-ray diffraction, and heating experiments to study three pieces (two "bright" and one "dull"; pers. commun., 1997) of shungite. The properties of shungite remained constant during heating to 850°C, and even at 2900°C the samples that were presumably type-I shungite did not graphitize; in the terminology of Franklin (1951), they consist of non-graphitizing carbon.

Many studies have been made of the structural characteristics of the carbon in the Shunga district. Type-I shungite has been reported as X-ray amorphous by Usenbaev *et al.* (1977) and poorly ordered by Grew (1974). High-resolution transmission electron microscopy (HRTEM) indicates that some structure exists, primarily in the form of slightly curled graphite-like layers (Buseck & Huang 1985). Jehlicka & Rouzaud (1993) commented on the inhomogeneity, as did Buseck & Huang. There are small regions (a few tenths of a nanometer across) of material that shows no structure, even when imaged using HRTEM. Kovalevski (1994) and Yushkin (1994) reported that the most characteristic feature of the carbon is a globular character, with units sized up to 10 nm across.

EXAMPLES OF OCCURRENCES OF HIGH-CARBON CONCENTRATIONS

Rocks from several areas have been mined for their carbon. Some, like the deposit at Shunga that contains shungite of types I and II, have been valued for the high grade of their carbon. However, the proven reserves of type-I and -II rocks are too low for current commercial purposes. In addition, this deposit is legally protected against exploitation because of its geological uniqueness. Other deposits, such as those at Zazhogino and Maksovo (shungite type-III), have been worked to recover rocks containing roughly 30 wt% carbon. They consist largely of carbon and quartz and have useful industrial properties. We will consider these areas in sequence as examples of the features of this district.

Shunga

The oldest and best known mine is at Shunga. It is located in the northern part of the Zaonezhsky Peninsula between lakes Putkozero and Valgmozero, too small to show on Figure 3. It lies in the northeastern part of the Onega structure, within the upper part of the greenschist-facies Ludicovian rocks.

The major rock types are massive carbonaceous dolomite and lydite. The latter contains about 95 wt% finely crystalline quartz, 2 to 4 wt% carbon, and about 1.5 wt% sericitic mica and metamorphic biotite. The lydite (shungite type-V; Table 1) is dense, has a conchoidal fracture, Mohs hardness of 7, and a density of 2.65 g/cm^3. According to Galdobina (1987), it is in a massive hydrothermal structure that cuts the dolomite and contains dolomite xenoliths. The lydite contains fractures filled with quartz, calcite, and "gumbellite" (secondary, fibrous sericite). The dolomite is interbedded with lydite and type-II material. The dolomite is dark gray to black, finely crystalline, and contains 2 to 7 wt% reduced carbon as well as minor mica, quartz, and sulfides (Sokolov & Kalinin 1975).

Various types of shungite rocks are exposed near the entrance of an adit at Shunga (Fig. 6). The most striking feature is a narrow, heavily jointed, seam-like layer of type-I shungite. The layer pinches and swells from roughly 8 to 50 cm and is continuous across approximately 30 m of exposure. It appears conformable, much like a typical metamorphosed sediment.

The rocks immediately above and below the seam contain appreciably less carbon and are classified

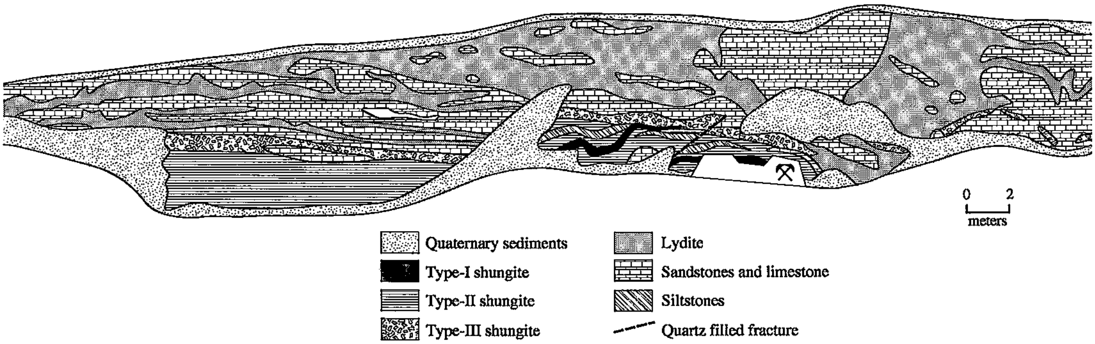

FIG. 6. Schematic geological cross-section of the Shunga region. The limestone symbols show position only and not orientation. The Shunga mine entrance is marked with crossed hammers (after Popov 1979).

as type-II shungite (Fig. 5b, Table 1). They contain pronounced, roughly orthogonal joints (much like cleats in coal) rather than being massive. The joint surfaces are heavily coated with films of yellow jarosite as a weathering product of the accessory sulfides in the shungite. The contact between the two types of layers is sharp (<1 mm) and, in most places, is defined by what appears to be a bedding plane (although it might be called a vein wall if it were vertical). The thickness of the type-II material is from 2 to 4 m (Sokolov & Kalinin 1975). It contains between 40 and 75 wt% carbon and the accessory minerals quartz, sericite, and biotite. It is cut by veinlets of quartz, calcite, and "gumbellite".

The seam of type-I shungite is the probable source of the sample in which Buseck *et al.* (1992) found fullerenes. On the basis of the results of Daly *et al.* (1993), it was suggested by Ebbesen *et al.* (1995) and contested by Buseck & Tsipursky (1995) that lightning was the probable source of the fullerenes. The type-I shungite here is overlain by 5 to 10 m of rocks. There is no evidence, either within the sample or in the field, of the pockets of formerly molten material that are typical products of lightning strikes. In addition, the probability of accidentally selecting such a sample from the mass of rock seems vanishingly small, and the thin veinlet character of the fullerene-bearing material is in marked contrast to the rounded to cylindrical shapes of lightning channels and fulgurites.

Zazhogino

An open cut of a working type-III shungite deposit occurs at Zazhogino, roughly 20 km from Shunga. At Zazhogino, there is a massive carbon-rich lens with dimensions ~200 × 250 × 50 m (level 2 of the cross section, Fig. 2). The rock contains 25 to 40 wt% carbon, with fine-grained muscovite, albite, quartz, sericite, minor pyrite, and "gumbellite" in veinlets. Bulk analysis gives 50 to 65 wt% SiO_2 and between 2 and 4 wt% K_2O. Drill holes show a similar underlying body that contains Na in place of K (level 1 of the cross section).

Stratigraphically, the Zazhogino lens is ~150 m below the Shunga deposit. Between them lie layers of tuffs, dolomites, bedded sulfide ores as well as basalt sills and flows (Fig. 2) and several carbonaceous lenses like that at Zazhogino.

Maksovo

The Maksovo deposit contains the same massive host-rocks as does Zazhogino, except that at Maksovo they are intensely brecciated. The deposit measures approximately 500 × 500 × 100 m; the southeastern part is exposed as a result of former mining, and the remainder has been defined through drilling at 25-m centers (Fig. 7). It is located on the hanging wall adjacent to an almost vertical normal fault with a roughly 200-m throw. The breccia fragments are cemented by veinlets containing elevated levels of carbon within quartz. The entire area is truncated by the fault and, as shown by the drilling, is underlain by carbonaceous limestone. Laterally adjacent layers do not form outcrops, but they have the same mineral assemblages as at Maksovo, except that they are free of carbon.

At Maksovo, there is an approximately vertical veinlet of glassy carbon (type-I shungite). The veinlet (Fig. 8) is located about 5 m from the fault; the two are roughly parallel. It is 3 cm wide and is exposed for about 20 m. It has well-defined, almost planar walls and is filled with extremely friable glassy carbon that can only be extracted as small (a few mm) flakes. The Maksovo type-I shungite has different mechanical properties from that at Shunga (Sokolov *et al.* 1984, Kovalevski 1994, Zaidenberg *et al.* 1996). Both are

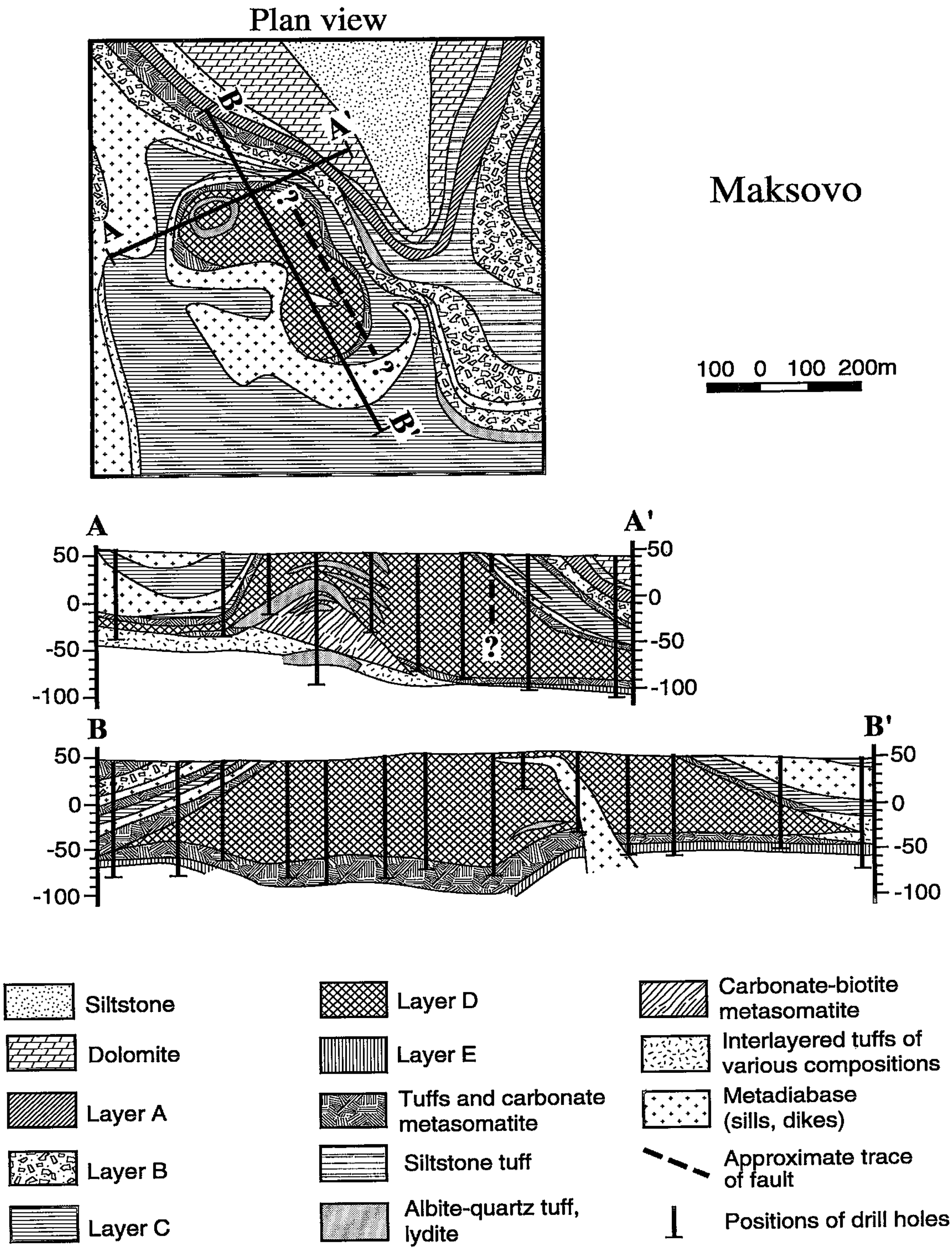

FIG. 7. Schematic geological plan view and cross-sections of the Maksovo region; the Maksovo quarry is located in the central part of the map. Layers A to E were mapped and apparently differentiated primarily by their carbon contents, but with an unspecified petrography (after Kupryakov & Mikhailov 1988).

FIG. 8. Narrow vein of glassy, type-I shungite from Maksovo. The sharp boundary is evident on the left side of the vein. The brittle character of the shungite combined with extensive sampling accounts for the recessed character of the vein.

similar on the X-ray scale, but they differ in the intensity distributions within the electron-diffraction rings, which indicate a stronger preferred orientation of the carbon in the Maksovo than in the Shunga material.

Comparison of the high-carbon rocks at Shunga and Maksovo

At Shunga, the highest-carbon rock occurs in an almost horizontal structure that resembles a seam and appears (to PRB) like a metamorphosed sediment, although the author (LPG) who is most familiar with the local geology believes it to be a metasomatized volcanic rock. At Maksovo, carbon that macroscopically appears to be almost identical occurs in a narrow vertical veinlet. It also has extremely well-defined walls, but in this instance it appears to cut across the surrounding rocks. The immediately adjoining rocks are massive, so that their attitudes are not known, whereas those above and below in the stratigraphic sequence display bedding roughly perpendicular to the veinlet.

The Shunga and Maksovo structures that contain type-I shungite are similar in the sharpness of their contacts and the unusual macroscopic appearance of their highly enriched contents of glassy carbon. The two structures differ in their orientations (horizontal *versus* vertical) and parallelness of their walls, with the Shunga body having a more irregular width, at least in the relatively restricted regions where it could be observed. The one at Shunga appears conformable, whereas the one at Maksova does not. It is hard to observe these two bodies and conclude anything other than a remobilized origin for the carbon.

Similar Occurrences

Within the greater Shunga region, similar rocks are found in several areas, including Nigozero, Berezovets (located 80 km from Shunga but beyond the map area), Munozero, Chebolaksha, Tolvuya, Spasskaya Guba, and near Lake Yandomozero (Fig. 3). Outside of Karelia, we know of no occurrences where carbon-rich rocks have similar field characteristics to those of the Shunga region.

Carbon Isotope Ratios

Analytical procedures

Selected samples were analyzed for their carbon isotopic ratios at the University of Wisconsin. Each sample was ground to a coarse powder and treated with aqua regia to remove sulfides and carbonates. The samples were rinsed and dried, weighed, mixed with CuO (an amount equal to ~100× the estimated weight of carbon in the sample), and sealed at vacuum in silica tubes. A ~10 mm^2 piece of silver foil was added to each tube to react with any remaining sulfides.

Prior to loading the samples, silica tubes were heated in air at 850°C for more than 10 h to remove carbon contaminants. The sealed sample tubes were baked at 840°C for ~16 h and annealed at 550°C for 8 h. After cooling, the evolved CO_2 was purified cryogenically and analyzed with a Finnigan MAT 251 mass spectrometer. Blanks were measured from silica tubes containing 500 mg of CuO but no sample. No measurable CO_2 (<0.5 μmol) was produced in these tests. Isotope ratios are presented in the standard per mil (‰) notation relative to the PDB standard (Table 2). Analyses of NBS–21 (spectroscopic graphite standard) yielded a $\delta^{13}C$ value of –28.25 ± 0.07‰ (Kitchen & Valley 1995).

Duplicate analyses were run of most samples, and the results in Table 2 show excellent analytical reproducibilities. Multiple chips were taken from several samples (samples M2b, Z3, Z6 from Maksovo and Zazhogino, and the Harvard sample from Shunga). The analyses of each of these samples show good precision, but they also show that minor but detectable heterogeneity exists within these rocks, with differences ranging from approximately 0.1 to 0.4‰.

TABLE 2. ISOTOPIC COMPOSITION AND PROPORTION OF CARBON, ROCKS FROM MAKSOVO, SHUNGA, AND ZAZHOGINO

Sample number	Description	$\delta^{13}C$ PDB	Precision*	% C yield
	Maksovo, Karelia			
M1a	Glassy carbon from vein (type-I shungite)	-26.92	(.94 .90)	81
M2b	Contact samples from vein (type-I shungite)	-27.05	(.03 .06)	63
M2b'	Contact samples from vein (type-I shungite)	-27.27	(.26 .27)	51
M4	Veined type-III shungite	-27.41	(.41 .41)	37
M5	Brecciated type-III shungite	-26.75	(.74 .76)	30
	Shunga, Karelia			
S1a	Carbon chips from "seam"; type-I shungite	-37.51	(.49 .52)	66
S2b	Massive type-II shungite from just below "seam"	-37.54	(.53 .54)	55
S4	Lydite – type-V shungite	-33.73	(.72 .74)	4
S5	Carbon-bearing dolomite	-37.45	(.43 .46)	43.5
	Type-I shungite from Harvard; collected by C. Hurlbut during the 1935 IGC	-37.47	(.47 .47)	73.5
	Type-I shungite from Harvard; collected by C. Hurlbut during the 1935 IGC	-37.57		63
	Zazhogino, Karelia			
Z1a	Massive type-III shungite	-26.71	(.70 .72)	28
Z1b	Massive type-III shungite	-27.00		30
Z3	Veinlet of quartz and type-I shungite in massive type-III shungite	-29.86	(.83 .88)	71
Z3'	Veinlet of quartz and type-I shungite in massive type-III shungite	-26.44	(.43 .44)	25.5
Z6	Fractures coated with slickenside graphite-like luster and gumbellite in type-III shungite	-26.73	(.72 .74)	30
Z6'	Fractures coated with slickenside graphite-like luster and gumbellite in type-III shungite	-26.51	(.50 .52)	33
Z7	Massive type-III shungite	-26.55	(.53 .56)	34

* Duplicate analyses were run for all but two samples; the numbers in parentheses indicate the places behind the decimal points and reflect the reproducibility of duplicate analyses.

Observations

Figure 9 shows the $\delta^{13}C$ values for samples collected by the authors during the summer of 1995 plus one collected by Dr. C. Hurlbut during the 1935 International Geological Congress. All are from either Maksovo, Shunga, or Zazhogino, the areas discussed in this paper. The map (Fig. 3) shows the localities, and brief descriptions of rock types are given in Table 2.

The compositions are tightly grouped by deposit and range between –26.43 and –37.57‰ PDB. Striking features of our results are their bimodal distribution (–26.9 ± 0.5 and –37.5 ± 0.1‰, with only two intermediate samples) and their consistency for each of these three locations, independent of the rock type. Thus, the isotopic compositions cluster by locality rather than shungite type. Maksovo and Zazhogino are of roughly the same age, whereas the rocks from the Shunga locality are younger (Fig. 2).

There have been several previous measurements of the isotopic composition of carbon in the rocks from the greater Shunga region. The first was by Rankama (1948), who investigated a sample of type-I shungite from the Shunga deposit and obtained a value of –42.1‰ PDB. Sokolov & Kalinin (1975) analyzed 13 shungite samples from the Maksovo, Shunga, and Zazhogino deposits and found values ranging from –21.4 to –39.9 for types-II, -III and -IV rocks and from –23.6 to –38.4‰ for type-I rocks. Chukhrov *et al.* (1984) analyzed nine samples from unspecified localities in the Lake Onega region and reported values from –35.9 to –41.9‰. Finally, Galdobina (1987) and Galdobina *et al.* (1995) studied 57 samples from the general Shunga region and reported values from –17.4 to –39.5‰. Their values also have a roughly bimodal distribution, with values centered at –26.4 and –37.6‰.

Each of the above authors or groups interpreted their data regarding origin of the rocks, but there is no consensus. Rankama (1948) and Chukhrov *et al.* (1984) interpreted their results as favoring a biogenic origin, whereas Sokolov & Kalinin (1975) took no stand, and Galdobina (1987) and Galdobina *et al.* (1995) interpreted their data as indicating a volcanic origin, with the more abundant higher-$\delta^{13}C$ samples being earlier than ones having the lower $\delta^{13}C$.

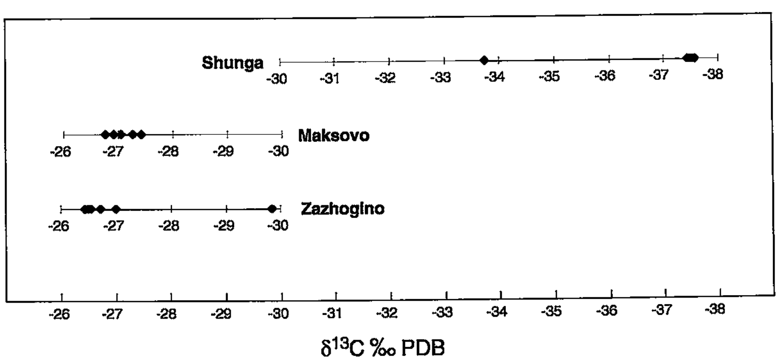

FIG. 9. Values of $\delta^{13}C$ for samples collected by the authors from Maksovo, Shunga, and Zazhogino during the summer of 1995, plus a sample of shungite collected by Dr. C. Hurlbut during the 1935 International Geological Congress.

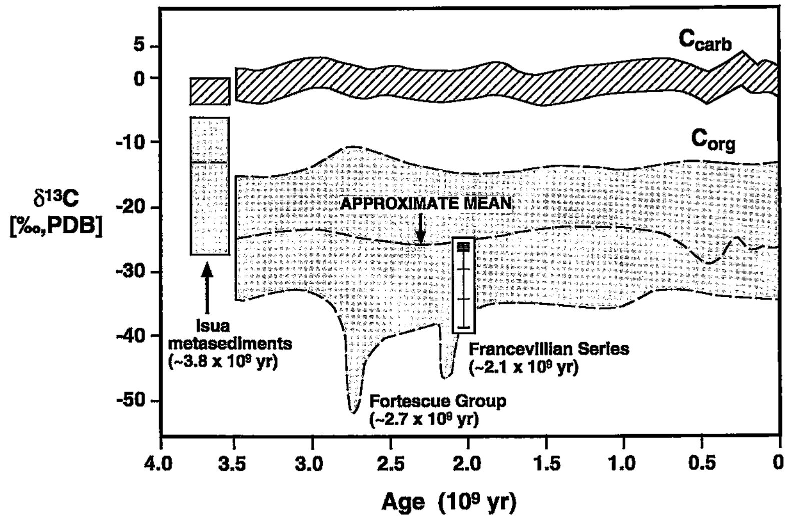

FIG. 10. Plot showing two "excursions" of isotopically light organic carbon that occurred in the Proterozoic (after Schidlowski 1987). The carbon isotopic compositions from the Shunga region are in the small vertical box inset near the Francevillian "excursion." The most strongly negative values are from the Shunga locality.

DISCUSSION

Petroleum, coal, solid bitumens, and graphite are well known to occur in carbon-rich districts. These materials differ in essential characteristics from the rocks found at Shunga, but there may be relationships. The Shunga rocks are poor in hydrocarbons [Mishunina & Korsakova (1977) and Bondar *et al.* (1987) indicated that they contain 0.06 to 0.17 wt% of organic matter] whereas, in marked contrast, the unmetamorphosed fossil fuels are rich in hydrocarbons. A closer relation may exist with districts that contain flake graphite, such as those in Sri Lanka, the Ruby Range in Montana, Llano Uplift in Texas, New Hampshire, and the Adirondacks, New York (Cameron & Weiss 1960) on the one hand, or the impsonite deposits of Oklahoma and the gilsonite dikes of Utah. Both impsonite and gilsonite are bitumens, *i.e.*, they are amorphous, carbon-rich solids that formed from pre-existing organic deposits.

The graphite districts mentioned above clearly experienced metamorphism above 500°C (*e.g.*, Valley & O'Neil 1981, Rumble & Hoering 1986, Kitchen & Valley 1995), whereas the impsonite and gilsonite formed at lower temperatures, presumably below ~250°C. In the gilsonite and impsonite deposits, carbon was presumably distilled from underlying organic-matter-rich oil shales. Temperatures were adequate to mobilize the carbon and move it to its current locations, but they were not sufficiently high to allow crystallization of graphite. A similar process might have contributed to forming the graphitic areas, except that higher temperatures were reached. Fluids rich in CO_2, CH_4, or both could have mobilized and transported the carbon from its original sites to that of deposition (Rumble & Hoering 1986, Rumble *et al.* 1986).

The Shunga deposits presumably formed at temperatures intermediate to those at which impsonite or gilsonite and flake graphite formed. Heating during regional metamorphism of finely disseminated hydrocarbons, possibly of biogenic origin, could have resulted in maturation of the reduced carbon that is dispersed throughout the dolomitic and lyditic rocks (*cf.* Dunn & Valley 1992); carbon-rich fluids, presumably generated by local sources of heat such as the diabase dikes and sills, concentrated and then deposited almost pure carbon in localized regions such as the "seam" at Shunga and the veinlet at Maksovo. The presence of glassy (type-I) carbon in veinlets indicates that it was remobilized and then precipitated in these new locations.

The range of carbon-isotope values for samples of shungite is similar to that of petroleum, natural gas, coal, and most animal and vegetable matter (Deines 1980a, Hoefs 1982, Hayes *et al.* 1983, Schidlowski *et al.* 1983, Schidlowski 1987). The cause of these uniformly low values is believed to be isotopic fractionation during photosynthesis; low $\delta^{13}C$ values in this range are generally accepted as proof of a biogenic origin. A possible exception is provided by a small percentage of diamonds that formed in the mantle and by carbon from some meteorites (Deines 1980b). These rare low-$\delta^{13}C$ values may represent extreme distillation-induced effects or subducted carbon that was originally of biogenic origin. In the case of a distillation mechanism, only small amounts of carbon with this composition could be formed. If this were an important process, a much larger residue with values significantly above –7‰ would exist elsewhere, undetected, in the mantle (Valley 1986). The carbon isotope ratios of meteorites form by a variety of processes, including spallation, not duplicated on Earth. There is no suggestion or indication that the 25×10^{10} tonnes of carbon in Karelia is meteoritic in origin.

The values of the $\delta^{13}C$ below –37‰ are restricted to Shunga and are lower than most organic matter. At certain discrete times in the Precambrian, such low values were common; values below –40‰ occur in sediments on several shields in tightly defined age spikes at 2.1 and 2.7 Ga (Strauss 1986, Schidlowski 1987) (Fig. 10). The 2.1-Ga event is similar in age to the shungites in this study and is also recognized in the Francevillian Series of Gabon.

The homogeneity in $\delta^{13}C$ that occurs at each deposit provides evidence linking the different types of shungite. At Shunga, all samples but one have a $\delta^{13}C$ value of –37.51 ± 0.05‰. Thus the type-I and type-II shungites have the same, unusually low value. Similar relations exist at Maksovo, where the type-I and type-III shungites have the same $\delta^{13}C$, –27.02 ± 0.37‰, and at Zazhogino, where all but one sample average –26.67 ± 0.20‰. These results indicate that all the reduced carbon in each area has a similar origin and argue against the possibility that cross-cutting varieties of shungite might have an origin unrelated to the other forms of reduced carbon. Two hypotheses result from this observation: 1) all of the carbon in each area was derived *in situ* from the same source, with cross-cutting veins representing locally remobilized carbon, or 2) all of the carbon for a given area was introduced from a single source. A third hypothesis, that the reduced carbon formed by a variety of processes and was subsequently homogenized by metamorphism, is unlikely because it would require that some of the carbon originally had an even more extreme $\delta^{13}C$ value, below –37.5‰, and also because graphite is highly resistant to isotopic exchange, even during granulite-facies metamorphism (Kitchen & Valley 1995).

If all of the carbon is allochthonous and of an abiogenic origin, then the mass balance of producing such a large, low-$\delta^{13}C$ district requires a source of carbon unlike any that is known on Earth. Conversely, if most of the carbon formed biologically and is syngenetic with enclosing sediments, then small amounts might be remobilized by metamorphism with little or no isotopic fractionation, and all of the observed relations are explained.

The few samples from the Shunga region that have values above –20‰ (reported by others) are probably the result of small amounts of mixing with inorganic (carbonate-derived) carbon that has a value near 0‰. Dolomite adjacent to the shungite would be a potential source of such carbon. Carbon that is originally of biogenic origin could also evolve to higher $\delta^{13}C$ values by maturation and devolatilization of isotopically lighter CH_4 or by exchange with high $\delta^{13}C$ carbonate (Valley & O'Neil 1981, Kitchen & Valley 1995).

The above biogenic–metamorphic interpretation is at odds with the interpretation of the field observations by LPG, who believes the evidence indicates an abiogenic, endogenic origin for shungite rocks.

The Shunga Deposits in a Global Context

The period around roughly 2 Ga, approximately when the Shunga deposits formed, was one of dynamic change on Earth. It was a time of global-scale collision of microcontinents to form modern-sized continents, resulting in the development of extensive stable platforms that could collect and preserve organic sediments (Des Marais 1994). The same period saw changes in the concentrations of atmospheric O_2 and CO_2, an increase in eukaryotic organisms, and profound reconfigurations of the ocean basins (Des Marais *et al.* 1992, Des Marais 1994, 1996, Rye *et al.* 1995, Grotzinger 1996).

Karhu & Holland (1996) pointed out that between 2.22 and 2.06 Ga, carbonate sediments in a wide range of localities worldwide experienced a sudden and unusually large positive excursion of their $\delta^{13}C$ compositions followed by an equally steep decline. They interpreted these as global effects and the result of an abnormally high rate of deposition of biogenic carbon, which, in turn, was the consequence of an unusually high rate of O_2 production in the atmosphere. Other evidence that the O_2 content of the atmosphere underwent a substantial increase during this period includes the oxidation state of paleosols, the geochemistry of uranium, and the occurrence of red beds (Holland & Beukes 1990, Kasting *et al.* 1992, Holland 1994). Karhu (1993) estimated that the total excess O_2 produced during this restricted but critical period was between 12 and 22 times that of the current inventory of oxygen in the atmosphere.

Few organic-matter-rich stratigraphic units have been identified from this time period, although they are known from both earlier and later times. It is conceivable that this gap is simply the result of a combination of limited preservation and sampling of such ancient rocks. However, the Shunga rocks formed close to this critical period, and it seems quite possible that they actually formed during that time, as did the extensive black shales of the Francevillian Series of Gabon (Bros *et al.* 1992). Moreover, as pointed out by Schidlowski (1987) and Gauthier-Lafaye & Weber (1989), the organic carbon from the Francevillian is unusually light, as is that for the Shunga region, in apparent complementary fashion to the carbonate $\delta^{13}C$ excursion. These observations make precise ages for the Shunga rocks of special interest; work is in progress to obtain such dates.

Except for a few periods of episodic increases, the proportion of organic carbon that was buried in sediments relative to carbonate has increased only slowly with time. However, the fraction of buried organic carbon peaked between 2.2 and 2.0 Ga (Karhu & Holland 1996), the period when the host formations for the Shunga deposits formed. It is clear that these deposits developed during a critical transitional period in the history of our planet, thus giving them a geological significance that adds to the fascination of the intriguing character of their unusual carbon.

Conclusions

The greater Shunga region is remarkable for the large amount of elemental carbon in Proterozoic (2.0 to 2.1 Ga) rocks. Some rocks appear to be unique because of their glassy, amorphous form. Veinlets of glassy carbon suggest that there was extensive remobilization, perhaps under the influence of volcanism or contact metamorphism. The carbon is, in general, isotopically light and ranges between –26.43 and –37.57‰ PDB. The detailed carbon isotopic compositions correlate with local area rather than rock type, suggesting that veins and host-rock carbon are related at each locality. This correlation indicates that all reduced carbon at each locality has the same genesis, and that either shungite veins are remobilized carbon derived from adjacent layers, or all carbon in these rocks has been introduced from some unknown external source. The age, local mobilization, and isotopic composition of the shungite rocks appear (to JWV and PRB) to indicate early, abundant life in the region. On the other hand, LPG interprets the field and isotopic data as indicating an abiogenic origin.

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References

Artamonov, V.S. & Kekkonen, A.P. (1935): *Shungite in the Past and at Present.* "Kirja", Petrozavodsk, Russia (in Russ.).

Bondar, E.B., Klesment, I.R. & Kuusik, M.G. (1987): Investigation of the structure and genesis of shungite. 1. The composition of extracts and thermal dissolution and hydrogenation products. *Oil Shales* N4/4, 377-393.

Borisov, P.A. (1956): *Karelian Shungites.* State Publishing House of Karelian-Finnish Republic, Petrozavodsk, Russia (in Russ.).

Bros, R., Stille, P., Gauthier-Lafaye, F., Weber, F. & Clauer, N. (1992): Sm–Nd isotopic dating of Proterozoic clay material: an example from the Francevillian sedimentary series, Gabon. *Earth Planet. Sci. Lett.* **113**, 207-218.

Buseck, P.R. & Huang, Bo-Jon (1985): Conversion of carbonaceous material to graphite during metamorphism. *Geochim. Cosmochim. Acta* **49**, 2003-2016.

________ & Tsipursky, S.J. (1995): Origins of fullerenes in rocks (response). *Science* **268**, 1635.

________, ________ & Hettich, R. (1992): Fullerenes from the geological environment. *Science* **257**, 215-217.

Cameron, E.N. & Weiss, P.L. (1960): Strategic graphite. *U.S. Geol. Surv., Bull.* **1082-E**, 201-321.

Chukhrov, F.V., Yermilova, L.P. & Nosik, L.P. (1984): On the isotopic composition of carbon in epigenetic graphites. *In* Syngenesis and Epigenesis in the Formation of Mineral Deposits (A. Wauschkuhn, C. Kluth, R.A. Zimmerman, eds.). Springer-Verlag, Berlin, Germany (130-137).

Cornelius, C.D. (1987): Classification of natural bitumen: a physical and chemical approach. *In* Exploration for Heavy Crude Oil and Natural Bitumen (R.F. Meyer, ed.). *Am. Assoc. Petroleum Geol., Studies in Geology* **25**, 165-174.

Daly, T., Buseck P.R., Williams P. & Lewis C.F. (1993): Fullerenes from a fulgurite. *Science* **259**, 1599-1601.

Deines, P. (1980a): The isotopic composition of reduced organic carbon. *In* Handbook of Environmental Geochemistry **1** (P. Fritz & J.C. Fontes, eds.). Elsevier, Amsterdam, The Netherlands (239-406).

________ (1980b): The carbon isotope composition of diamonds: relationship to diamond shape, color, occurrence and vapor composition. *Geochim. Cosmochim. Acta* **44**, 943-962.

Des Marais, D.J. (1994): Tectonic control of the crustal organic carbon reservoir during the Precambrian. *Chem. Geol.* **114**, 303-314.

________ (1996): The biogeochemical carbon cycle and the evolution of the Proterozoic atmosphere. *Geol. Soc. Am., Abstr. Programs* **28**, A218.

________, STRAUSS, H., SUMMONS, R.E. & HAYES, J.M. (1992): Carbon isotope evidence for the stepwise oxidation of the Proterozoic environment. *Nature* **359**, 605-609.

DUNN, S.R. & VALLEY, J.W. (1992): Calcite–graphite isotope thermometry: a test for polymetamorphism in marble, Tudor Gabbro aureole, Canada. *J. Metamorphic Geol.* **10**, 487-501.

EBBESEN, T.W., HIURA, H., HEDENQUIST, J.W., DE RONDE, C.E.J., ANDERSEN, A., OFTEN, M. & MELEZHIK, V.A. (1995): Origins of fullerenes in rocks. *Science* **268**, 1634-1635.

FERSMAN, A.E. (1922): *Geochemistry of Russia.* Theoretical Chemistry Publishing House, Moscow, Russia (in Russ.).

FRANKLIN, R.E. (1951): Crystallite growth in graphitizing and non-graphitizing carbons. *Proc. R. Soc. London* **A209**, 196-218.

GALDOBINA, L.P. (1987): Metallogeny of shungite-bearing and shungitic rocks of the Onega basin. *In* Metallogenia of Karelia (V.A. Kostin, ed.). Proc. Inst. Geol., Petrozavodsk, Russia (in Russ.; 100 -113).

________ (1993): Shungite. *In* Precambrian Industrial Minerals of Karelia (V. Shchiptsov, ed.). Inst. Geol., Karelian Res. Centre, Russian Acad. Sci., Petrozavodsk, Russia (45-50).

________, KALININ, YU.K. & BOGACHEVA, M.P. (1995): Isotopic carbon fractionation of shungite rocks of Karelia. *Proc. 14th Symp. on Isotopic Geochemistry*, 47-48 (in Russ.).

GAUTHIER-LAFAYE, F. & WEBER, F. (1989): The Francevillian (Lower Proterozoic) uranium ore deposits of Gabon. *Econ. Geol.* **84**, 2267-2285.

GENERALOV, M.E. (1995): Ore mineralogy of the Karelian shungites. *In* Mineral Deposits: from their Origin to their Environmental Impacts (J. Pasava, B. Kribek & K. Zák, eds.). *Proc. 3rd Biennial SGA Mtg.* (*Prague*). A.A. Balkema, Rotterdam, The Netherlands (739-742).

GOLUBEV, A.I. & AKHMEDOV, A.M. (1995): Black schist key beds in the early Proterozoic complexes of the Baltic Shield. *In* Precambrian of Europe: Stratigraphy, Structure, Evolution and Mineralization (V.A. Glebovitski & A.B. Kotov, eds.). *Assoc. Eur. Geol. Soc., 9th Meet.* (*St. Petersburg*), 37 (abstr.).

GREW, E.S. (1974): Carbonaceous material in some metamorphic rocks of New England and other areas. *J. Geol.* **82**, 50-73.

GROTZINGER, J.P. (1996): Constraints on the composition of Precambrian seawater from the record of carbonates and evaporites. *Geol. Soc. Am., Abstr. Programs* **28**(7), A-218.

HAYES, J.M., KAPLAN, I.R. & WEDEKING, K.W. (1983): Precambrian organic geochemistry, preservation of the record. *In* Earth's Earliest Biosphere: its Origin and Evolution (J.W. Schopf, ed.). Princeton University Press, Princeton, N.J. (93-134).

HOEFS, J. (1982): Isotope geochemistry of carbon. *In* Stable Isotopes (H.L. Schmidt, H. Förstel & K. Heinzinger, eds.). Elsevier, Amsterdam, The Netherlands (103-113).

HOLLAND, H.D. (1994): Early Proterozoic atmospheric change. *In* Early Life on Earth (S. Bengtson, ed.). Columbia University Press, New York, N.Y. (237-244).

________ & BEUKES, N.J. (1990): A paleoweathering profile from Griqualand West, South Africa: evidence for a dramatic rise in atmospheric oxygen between 2.2 and 1.9 BYBP. *Am. J. Sci.* **290-A**, 1-34.

INOSTRANTSEV, A.A. (1879): New extreme example in the series of amorphous carbon. *Gornii Journal* **2**, 314-342 (in Russ.).

IVANKIN, P.F., GALDOBINA L.P. & KALININ YU.K. (1987): Shungites: problems of genesis and classification. *Soviet Geology* **N12**, 40-47 (in Russ.).

JEHLICKA, J. & ROUZAUD, J.N. (1993): Transmission electron microscopy of carbonaceous matter in Precambrian shungite from Karelia. *In* Bitumens in Ore Deposits (J. Parnell, H. Kucha & P. Landais, eds.). Springer Verlag, Berlin, Germany (53-60).

KALININ, YU.K. (1990): Shungite rocks: structure, properties and fields of application. *Proc. All-Union Mineral. Soc.* **CXIX**(5), 1-8 (in Russ.).

KARHU, J.A. (1993): Paleoproterozoic evolution of the carbon isotope ratios of sedimentary carbonates in the Fennoscandian Shield. *Geol. Surv. Finland, Bull.* **371**.

________ & HOLLAND, H.D. (1996): Carbon isotopes and the rise of atmospheric oxygen. *Geology* **24**, 867-870.

KASTING, H.F. HOLLAND, H. D. & KUMP, L.R. (1992): Atmospheric evolution: the rise of oxygen. *In* The Proterozoic Biosphere: a Multidisciplinary Study (J.W. Schopf & C. Klein, eds.). Cambridge University Press, Cambridge, U.K. (159-163).

KHAVARI-KHORASANI, G. & MURCHISON, D.G. (1979): The nature of Karelian shungite. *Chem. Geol.* **26**, 165-182.

KINOSHITA, K. (1988): *Carbon: Electrochemical and Physicochemical Properties.* John Wiley and Sons, New York, N.Y.

KITCHEN, N.E. & VALLEY, J.W. (1995): Carbon isotope thermometry in marbles of the Adirondack Mountains, New York. *J. Metamorphic Geol.* **13**, 577-594.

KOVALEVSKI, V. (1994): Structure of shungite carbon. *Russ. J. Inorg Chem.* **39**, 28-32.

________, ROZHKOVA, N., ZAIDENBERG, A. & YERMOLIN, A. (1994): Fullerene-like structures in shungite and their physical properties. *Molecular Materials* **4**, 77-80.

KUPRYAKOV, S.V. & MIKHAILOV, V.P. (1988): Zazhogino locality of shungite rocks. *In* New Points in the Geology of the North-western Part of Russia (V.V. Proskuryakov, ed.). Nauka, Moscow, Russia (in Russ.; 79-86).

LEVCHENKOV, O.A., LOBACH-ZUCHENKO, S.B., SERGEYEV, S.A. & ROBONEN, V.I. (1990): Modern geochronology of early Precambrian of Karelia. *In* Geology and Geochronology of Precambrian of Eastern European Platform (S.B. Lobach-Zuchenko & E.V. Bibikova, eds.). Nauka, Leningrad, Russia (in Russ.; 72-80).

LOBZOVA, R.V. & GALDOBINA, L.P. (1987): About shungite forming process in Karelia. *In* New Kinds of Nonmetallic Raw Materials (V.P. Petrov, ed.). Nauka, Moscow (in Russ.; 51-57).

MEYER, R.F. & DE WITT, W., JR. (1990): Definition and world resources of natural bitumens. *U.S. Geol. Surv., Bull.* **1944**.

MEYERHOFF, A.A. & MEYER, R.F. (1987): Geology of heavy crude oil and natural bitumen in the USSR, Mongolia and China. *In* Exploration for Heavy Crude Oil and Natural Bitumen (R.F. Meyer, ed.). *Am. Assoc. Petroleum Geol., Studies in Geology* **25**, 31-101.

MISHUNINA, Z.A. & KORSAKOVA, A.G. (1977): Geochemistry of kerogen in graphite and shungite of shales and carbonates of the Proterozoic in South Karelia. *Sovyetskaya Geologiya* **N3**, 40-54 (in Russ.).

PARFEN'YEVA, L.S., SMIRNOV, I.A., ZAIDENBERG, A.Z., ROZHKOVA, N.N. & STEFANOVICH, G.B. (1994): Electric conductivity of shungitic carbon. *Fiz. Tverd. Tela (St. Petersburg)* **36**(1), 234-236 (in Russ.).

PARNELL, J., CAREY, P.F. & BOTTRELL, S.H. (1994): The occurrence of authigenic minerals in solid bitumens. *J. Sed. Res.* **A64**, 95-100.

PARRA, J.B., DE SOUSA, J.C., PIS, J.J., PAJARES, J.A. & BANSAL, R.C. (1995): Effect of gasification on the porous characteristics of activated carbons from a semianthracite. *Carbon* **33**, 801-807.

POPOV, V.E. (1979): *Volcanic-sedimentary Deposits*. Nedra, Leningrad, Russia (in Russ.).

PUHTEL, I.S., ZHURAVLEV, D.Z., ASHIHMINA, N.A., KULIKOV, V.S. & KULIKOVA, V.V. (1992): Sm–Nd age of the Suisarian of Baltic shield. *Dokl. Akad. Nauk Russia* **326**, 706-711 (in Russ.).

RANKAMA, K. (1948): New evidence of the origin of Pre-cambrian carbon. *Geol. Soc. Am., Bull.* **59**, 389-416.

RUMBLE, D., III, DUKE, E.F. & HOERING, T.C. (1986): Hydrothermal graphite in New Hampshire: evidence of carbon mobility during regional metamorphism. *Geology* **14**, 452-455.

________ & HOERING, T.C. (1986): Carbon isotope geochemistry of graphite vein deposits from New Hampshire, U.S.A. *Geochim. Cosmochim. Acta* **50**, 1239-1247.

RYE, R., KUO, P.H. & HOLLAND, H.D. (1995): Atmospheric carbon dioxide concentrations before 2.2 billion years ago. *Nature* **378**, 603-605.

SCHIDLOWSKI, M. (1987): Application of stable carbon isotopes to early biochemical evolution on Earth. *Annu. Rev. Earth Planet. Sci.* **15**, 47-72.

________, HAYES, J.M. & KAPLAN, I.R. (1983): Isotopic inferences of ancient biochemistries: carbon, sulfur, hydrogen & nitrogen. *In* Earth's Earliest Biosphere: Its Origin and Evolution (J.W. Schopf, ed.). Princeton Univ. Press, Princeton, N.J. (149-186).

SOKOLOV, V.A. & KALININ, YU.K. (1975): *Shungites of Karelia and Ways of their All-purpose Utilization.* Karelia, Petrozavodsk, Russia (in Russ.).

________, ________ & DUKKIYEV, E.F. (1984): *Shungites – New Carbonaceous Materials.* Karelia, Petrozavodsk, Russia (in Russ.).

SOLOVOV, V.K., TUPOLYEV, A.G., ZAIDENBERG, A.Z., ZVERYEV, A.A. & KALININ, YU.K. (1990): Electromagnetic spectral analysis of conducting composites. *In* MICC-90 Moscow Int. Composites Conf. (I.N. Fridlyander & V.I. Kostikov, eds.). Elsevier, London, U.K. (1343-1347).

STRAUSS, H. (1986): Carbon and sulfur isotopes in Precambrian sediments from the Canadian Shield. *Geochim. Cosmochim. Acta* **50**, 2653-2662.

SUDOVIKOV, N.G. (1937): Geological sketch of the Zaonezhye Peninsula. The Northern Excursion, XVII International Geological Congress, "Lengorlit" #2648, Leningrad, Russia (46-57).

TIMOFEYEV, V.M. (1924): About genesis of shungite from the Onega region. *Proc. Leningrad Soc. Naturalists* **39**(4), 40-50 (in Russ.).

USENBAEV, K., ZHUMALIYEVA, K., RUSKULBEKOVA, R. & KALININ, YU. (1977): Structure of the shungite-1. *Dokl. Acad. Sci. USSR, Earth Sci. Sect.* **232**, 185-188.

VALLEY, J.W. (1986): Stable isotope geochemistry of metamorphic rocks. *In* Stable Isotopes in High Temperature Geological Processes (J.W. Valley, H.P. Taylor, Jr. & J.R. O'Neil, eds.). *Rev. Mineral.* **16**, 445-489.

________ & O'NEIL, J.R. (1981): $^{13}C/^{12}C$ exchange between calcite and graphite: a possible thermometer in Grenville marbles. *Geochim. Cosmochim. Acta* **45**, 415-419.

VOLKOVA, I.B. & BOGDANOVA, M.V. (1986): Petrology and genesis of Karelian shungite – high-rank coal. *Int. J. Coal Geol.* **6**, 369-379.

VOLODICHEV, O.I. (1987) Metamorphism. *In* Geology of Karelia (V.A. Sokolov, *ed.*). Nauka, Leningrad, Russia (172-175).

YUSHKIN, N.P. (1994): Globular shungite structure: tunnel electron microscopic data. *Dokl. Russian Akad. Nauk* **337**, 800-803 (in Russ.).

ZAIDENBERG, A., KOVALEVSKI, V.V. & ROZHKOVA, N.N. (1995): Spheroidal fullerene-like carbon in shungite rock. *In* Recent Advances Chem. Phys. of Fullerenes and Related Materials. *Proc. Electrochem. Soc.* **95-10**, 126-130.

________, ROZHKOVA, N., KOVALEVSKI, V. & TUPOLEV, A. (1996): About fullerene-like structures of shungite carbon. *Russ. J. Phys. Chem.* **70**, 107-110.

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