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Primary organic matter and lithofacies of siliceous shungite rocks from Karelia

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Abstract: The genesis of carbon-rich rocks (shungite rocks) and accompanying phtanites (lydites) from the Early Proterozoic (2,1 - 2,0 Ga) of the Transonega Formation in Karelia (Eastern Fennoscandian Shield) is discussed. Some features of composition, structure and texture of these rocks as well as the structure of the deposits is described. Microtextures of lydites were studied by means of scanning electronic microscopy. The organogenic origin of primary sedimentary organic matter as well as the originally colloidal nature of silica could be confirmed.

Zusammenfassung: Die Bildung kohlenstoffreicher Gesteine (Schungitgesteine) und zusammen mit ihnen vorkommender Ftanite (Lydite) aus dem frühen Proterozoikum (2,1 - 2,0 Ga) der Transonega Formation Kareliens (Östlicher Fennoskandischer Schild) wird diskutiert. Merkmale der Zusammensetzung, Struktur und Textur dieser Gesteine ebenso wie der Aufbau der Lagerstätten werden beschrieben. Die Mikrot Texturen der Lydite wurden mittels Rasterelektronenmikroskopie (SEM) untersucht. Der organische Ursprung der primär sedimentierten organischen Substanz ebenso wie eine ursprünglich kolloidale Natur der Kieselsäure konnten bestätigt werden.

Introduction

Shungite is a noncrystalline organic matter which is in the meta-anthracitic stage of metamorphism. It occurs in dispersed and concentrated form in rocks and as aggregates in veins and veinlets. The term "shungite" was introduced by A. A. INOSTRANTSEV (1880) for a relatively pure carbon substance containing about 98 % of carbon. Shungite was first found in the Early Proterozoic metasedimentary rocks near the Karelian village Shunga in north-western Russia. (Fig.1). Crystallographically, shungite is a mineraloid because it is roentgenoamorphous.

The origin of shungite, its physical properties and other problems are discussed in many papers and monographs. However, the data is largely unavailable to international readers, since its majority were published in Russian language.

The origin of shungite is still a subject of debate. In the late 19th century shungite was called "Olonets anthracite" because it looks like coal. Later it was proved that shungite differs greatly in physicochemical structure properties from humus coal.

In 1924, V. M. TIMOFEYEV assumed that shungite was derived from sapropel. The dying-off and transformation products of protozoan algae were thought to have provided a source of shungite. The same substance was considered a source of pyrobitumens defined as mobile hydrocarbons formed under the influence of magmatic rock heat. In the course of migration they filled fractures and voids in host rocks, including parent rocks. The hypothesis was developed later by N. I. RYABOV (1935), K. RANKAMA

(1948), P. A. BORISOV (1956), V. A. USPENSKY et al. (1961, 1964), A. V. SIDORENKO et al. (1971), G. S. KALMYKOV (1974), Z. A. MISHUNINA (1978), O. A. RADCHENKO et al. (1979), N. A. LOPATIN (1983), V. I. GORLOV (1984), E. B. BONDAR et al. (1987) and S. I. ZHMUR et al. (1993).

An alternative hypothesis concerning the possible abiogenic origin of shungite was first presented in 1975 (KALININ et al. 1975). The conception was later supported by other investigators (GALDOBINA et al. 1986, IVANKIN et al. 1987, KUPRYAKOV et al. 1988). Their hypothesis assumes that deep gas emanations, which accompanied magmatic processes, provided a source of organic matter. According to one hypothesis option, this matter saturated the earlier formed sedimentary rocks; according to the other, it condensed on the way to the surface and precipitated in the form of asphalt-like material or an organomineral substance. Y. K. Kalinin was the only author who tried to prove the hypothesis. The main conclusions favouring the depth origin of the organic matter are based on the functional relation of $\delta^{13}\text{C}$ of shungite matter to the potassium modulus and on "direct proportional" relation between the concentration of shungite carbon and complex aluminosilicates.

Carbon-rich (shungite) rocks from the Early Proterozoic (2,1 - 2,0 Ga) Transonega Formation of Karelia (Eastern Fennoscandian Shield) (Fig. 2) have been considered as possible objects of mining activities because of their special properties (SOKOLOV & KALININ (Eds.) 1975, SOKOLOV, KALININ & DUKKIYEV (Eds.) 1984, SOLOVOV et al. 1990). The rocks have been classified according to their content of organic carbon (C_{org}) ranging from 20 to 80 %. Three deposits of shungite rocks were prospected in detail within the Onega synclinoria in recent times: Shunga, Maksovo and Zazhogino. Other promising localities are Kaleiskoje, Podsosonje, Kochkoma etc. (Fig. 3). All these shungite deposits are either dome-shaped or situated in anticline cores. At the margin of the domes and in the anticline cores carbon-rich rocks are replaced by bedded carbon-bearing siltstones, tuffs and dolostones as a rule. The nature of shungite rocks as well as the genesis of shungite deposits are presently under discussion (PHILIPPOV et al. 1994, BUSEK et al. 1997, MELEZHIK et al. 1999).

Characteristics of shungite rocks and structure of their deposits

The Shungite rock is a grey-black, pelitomorphic, fine-grained, homogeneous, massive, dense rock, that has a pronounced conchoidal fracture but no visible lamination. Parallel-epipedical compartmentation appears if $C_{\text{org}} > 45\%$. Increasing of grain size and primary lamination appears if $C_{\text{org}} < 20\%$. According to the methods used in petrography, like X-ray diffraction and electron microscopy, the main minerals of shungites are quartz, sericite, albite, chlorite, calcite, dolomite and pyrite (PHILIPPOV et al. 1994). The percentage of each single mineral in shungite rocks can vary considerably. To give an example, shungite rocks from the first member (stratigraphic unit) of the middle part of the Transonega Formation contain quartz, albite and chlorite as main mineral components, whereas shungites from the second member have sericite as main mineral.

The composition of shungite rocks has been thoroughly studied (Table 1):

SiO_2 predominates among the minerals forming - as a rule - more than one third of the total rock weight, Al_2O_3 yields from 4.3 to 8.5 wt%, and the oxides of Fe, Ca, Mg, K, Na follow in decreasing order. It should be mentioned that C_{org} does not show positive linear correlation coefficients to any of the oxides. According to microprobe analysis Si is evenly distributed in shungites, Fe and S however (pyrite

intercalations) less evenly. Correlation of Al with K and with Si (partly) is distinct, because of sericite, also of Mg with Al, because of chlorite, of Fe with S, because of pyrite (a part of Fe is contained in chlorite however). Thus shungite represents an aggregate of organic matter, quartz, sericite, chlorite, pyrite and rare carbonate. The size of single mineral grains is obviously a few micrometer only. According to the module diagrams published by PREDOVSKY (1970) and JUDOVICH et al. (1986), shungites are siliceous, clay-siliceous or clay-carbonate-siliceous sediments with an unusual high content (especially in Precambrian terms) of organic matter.

Calculation of the primary mineral composition of the Maksovo shungite deposit according to ROSEN's method (ROSEN 1970) yielded the following results: SiO₂: 66.8 wt.%, clay: 19.5 wt.%, carbonates: 4.8 wt.%, feldspars: 3.5 wt.%. Siliceous and clay constituents are also prevailing in other shungite beds. There is no correlation between organic matter and mineral components of shungites.

The dome-shaped deposits of the carbon-rich rocks have some specific features in respect to their structure and mineral composition. The main part of shungites is concentrated within them where the content of C_{org} rises up to 70 %. The rocks are brecciated and show fluid textures. Specific features of shungite deposits have been studied at the Maksovo deposit, because this deposit is less eroded than others and has moreover been prospected in detail. The dome-shaped deposit shows dimensions of 500 x 700 m at plan outline. Thickness of shungites is 120 m in the central part of the deposit but in the margin only up to 8 - 10 m. The distribution of C_{org} is uneven, increasing towards the center and the upper part of the dome. The carbon isotope ratio $\delta^{13}\text{C}$ in the deposit shows uneven distribution too: the central part of the dome has lighter C_{org} ($\delta^{13}\text{C} = -42.4 \text{‰ PDB}$) than the marginal part ($\delta^{13}\text{C} = -27.3 \text{‰ PDB}$; AKHMEDOV 1995). This can be explained by differentiation of a primary, organic-rich sediment. The SiO₂/Al₂O₃ ratio, characterized by an increase of the SiO₂ content, has the same tendency of increasing towards the central part of the deposit. More than 3/4 of the shungites at Maksovo show a surprisingly simple mineral composition: quartz, sericite, and a minor quantity of pyrite. The lower part of the deposit consists of carbon-bearing rocks with visible bedding, containing chlorite, phlogopite, talc and carbonates. The top of the deposit yields the lightest components of the original sediment, consisting of organic-clay and organic-siliceous parts. The presence of this top part is a main feature of a mature shungite dome. One more feature of a shungite deposit is the occurrence of phtanite lenses. Lydites and silicites form thin covers (Shunga and Maksovo deposits) or lenses (Maksovo and Zazhogino) - a characteristic, general structure of the deposits.

Petrographical investigations of the shungite texture by standard methods are useful sometimes, because thin sections (for transmitted light) must be very thin (less than 0.01 mm). BOGDANOVA was the first to use methods of coal petrography (observation in polarized, reflected light with oil immersion) for the shungite investigation (GORLOV & BOGDANOVA 1967). The main shungite types were recognized by spot inclusions in mineral matrix, films (pellicles) and lens-like intercalations. In the organic matter of the shungites a distinct anisotropy was found, similar to that of the organic matter of anthracite. If the content of C_{org} is close to 70 %, mineral components are present in the form of small, dispersed particles of quartz, mica and pyrite. By means of oil immersion and magnification x 665 KALMYKOV (1974) detected in shungite separate bands, lenses, fibres of the organic matter up to a size of 10 - 20 μm . The fibres form textures similar to those of some humic and sapropelitic coals. Lens-like and cell-like structures in shungites comparable to those in Palaeozoic humic coals were also detected also by VOLKOVA & BOGDANOVA (1986) by treating polished samples from Shunga locality with acid.

Shungites often show fluidal macro- and microtexture. During the prospection of the Shunga deposit, these fluidal textures and structures were observed on the walls of the pits and mines. Shungites have overflowed disintegrated beds of dolostones and carbon-bearing rocks (PHILIPPOV & ROMASHKIN 1996). Brecciated shungites are very widespread in the deposits, the matrix of these breccias being shungite or quartz. Fragments of these breccias are covered by organic matter. Migrated organic matter is also present as interstitial filling. In thin sections, the lumpy texture of the shungites is visible. Homogenous isometric clots of organic matter are separated from each other by chains of fine-grained quartz. The clots possibly consist of carbon-mineral aggregates - metamorphic organic clays and organic-siliceous complexes. Parts of the shungites with fluidal texture show features of plastic deformations: the clots are flattened, sometimes they have lens-like shape. Presence of indistinct microlamination is emphasized by thin, longitudinal segregations of quartz and sericite.

Accompanying lydites and silicites have globular or globular-clotted textures. Siliceous globules - up to 0.1 mm in size - are covered by organic matter and surrounded by carbon-quartz matrix. Carbon-rich silicites have the same lumpy textures as the shungites of the dome deposits. Frequently, the texture of the lydites shows features of plastic movements of matter - the clots are deformed, lengthened, and flattened with microlamination being visible.

According to petrography and microprobe data, therefore organic matter of shungites is closely related to mineral substances, but calculations of correlation do not show any significance. There are the following possible explanations for this phenomenon: (1) Sources of organic matter, silica and clay were independent. (2) The productivity of the sources was variable at different stages of sedimentation. (3) Interaction of organic matter and mineral substance depended on their composition and properties, which were changing in time. (4) Katagenic and metamorphic processes destroyed possible primary relationships between organic matter and other components of shungites. (5) Correlation is non-linear.

A possible source of the organic matter in shungites

The close association of the organic matter with cryptocrystalline mineral substance confirms adsorptional processes (KLUBOVA et al. 1986). In addition, there exists also migrated organic matter forming films and fillings of fractures. A part of the organic matter is present in the form of microfossils (KALMYKOV 1974, PHILIPPOV et al. 1994, ZHMUR et al. 1993).

Structural organic remains preserved in carbon-rich rocks are very rare. As a general rule organic matter of living organisms is preserved more often than their shape. Siliceous rocks - e.g. cherts, lydites - are much more suitable for the conservation of structural organic remains, caused by an early diagenetic replacement of micro-organisms by silica. For this reason microfossils were found in carbon-bearing siliceous rocks - in the lydites (cherts). Polishing and careful etching of the surface, that is investigated for possible microfossils, is necessary and it must be demonstrated that the filaments or sheaths are within the rock (ALTERMANN & SCHOPF, 1995). Classification of Precambrian microfossils has to rely on morphometrics and on morphological comparison to extant species. The main characteristics used in classification include: 1) shape and size of cells; 2) form of filament and thallus; 3) patterns of cell growth and division; 4) presence or absence of extracellular sheets or envelopes; 5) form of extracellular structures and of wall ornamentation; 6) presence or absence of colonial organisation. Schopf(1992) suggested that fossil septate filaments <1.5 µm wide be regarded as probable bacteria and those >3.5

µm wide as probable cyanobacteria. The range between these two classes is referred to as „undifferentiated prokaryotes“. There are numerous carbon films with regularly arranged holes, that can be distinguished as remains of Cyanophyta (PHILIPPOV et al., 1994, photos 14, 17). Microfossils which have been detected in shungites are regarded as remains of benthic Cyanophyta (ZHMUR et al. 1993). They are considered to have been living in the photic zone of a basin, the shungites containing them to have been formed in a shallow water environment but not from precipitated plankton in deep water environment like suggested by GLIKSON et al. (1989).

Benthic *Cyanophyta* can form complex microbial communities - cyanobacterial mats. At present time microbialites occur in shoreline marine and lacustrine environments. The productivity of modern cyanobacterial mats is up to 8 - 12 g/m² of C_{org} per day (COHEN et al. 1980). If productivity was similar in the Precambrian (LANIER 1986), Cyanophyta can be regarded as a probable source of C_{org} for the formation of Precambrian carbon-rich sediments, including the shungites.

Considering cyanobacterial mats as a possible source of C_{org} in shungites it is necessary to realize both their photosynthetic ability and the peculiarities of decomposition of organic matter in such "algal" mats as well. Anaerobic conditions beneath the surface have prevented the destruction of lipids and photosynthetic membranes of *Cyanophyta*. Such remains of membranes could be detected in sections of cyanobacterial mats a few mm under their surface by means of electron microscopy (GERASIMENKO & ZAVARZIN 1993). They are a possible source for the formation of kerogen.

Finds of molecular fossils in bitumen isolated by extraction from the shungites yielded identical hints: mixtures of fatty acids, for instance, as discovered in the bitumens show a composition which is characteristic for lipids of *Cyanophyta* (BONDAR et al. 1987). Syngenetic pyrite in shungites contains biomarkers which confirm that thermoacidophilic bacteria, cyanobacteria - "blue-green algae" - growing during the Early Proterozoic in a sulfidic, reducing environment (e. g. sabkha) can be regarded as a possible source of organic matter in shungites (MYCKE et al. 1987).

Microstructure of Shungites and Lydites

Mineral substance of carbon-rich rocks in shungite deposits consists of two parts: quartz and mica. According to modern concepts (MURAVYEV 1987, HVOROVA & DMITRIK 1972), the siliceous sediment is a hydrogel-opal containing up to 21 % and more of water during its diagenesis. During the catagenesis a process of dehydration and crystallization of the opal takes place. Firstly, the opal partly crystallizes as crystobalite and partly dehydrates, colloform structures of silica being formed. When the dehydration is almost completed, the opal disappears and the crystobalite turns into chalcedony and quartz. Subcolloform and crystalloform structures of silica form in this stage. It should be emphasized that jaspers have crystalloform and novaculite microstructures, but carbon-bearing phtanites preserve colloform and subcolloform structures (HVOROVA & VISHNEVSKAYA 1987).

Shungites and lydites have suffered greenschist conditions of metamorphism, silica being present in the form of quartz, but there are relics of colloform and subcolloform structures, sometimes also chalcedony. The structures can therefore be called metacolloform and metasubcolloform.

Structures of siliceous components of shungites show colloform features. The process of their development can be observed in the lydites, which originally accompany the shungites, but have less

carbon and no mica. Microtextures of silica and interrelation of carbon and siliceous matrix are shown in SEM photographs (Fig. 4, 5).

Metacolloform globular structure is shown in Fig. 4: tiny aggregates of globular and elongated silica are constitutional for this structure. Globules covered with carbon are formed in it. The carbon coatings are multilayered, and often not closed. It is possible to distinguish a "step by step" developmental process leading to paired globules and their aggregates: (1) Usually a coating of carbon forms an aggregate or a pair of globules. (2) Organic matter is then separated from the globules and removed to the margins of the aggregate. This is a stage with beginning crystallization and separation of the organic-silica gel.

Metacolloform structure with dehydration cracks of the organic-silica gel is shown in Fig. 5. This is an ideal picture of the colloform structure with globules, which are in different forming stages and are covered with carbon. A system of cracks is the result of the dehydration of the gel. Carbon films on the walls of the cracks indicate that the process of separation of organic and siliceous parts has been continued after cracking and condensation of the gel.

Thus, the siliceous component of shungites shows microstructures similar to siliceous rocks of chemogenic origin. Some colloform features characterize siliceous components of shungites and lydites, their colloid nature and the active interaction with organic matter becoming evident in this way.

Discussion

Formation of carbon-bearing carbonates, siliceous rocks (phtanites) and shungites took place during active volcanism, that is marked by numerous lava flows and tuff beds in the sequence. Accumulation of siliceous rocks is usually connected with submarine volcanism in Precambrian times (KALEDA 1987). Siliceous rocks were formed from silica solutions close to saturation. The process resulted in the formation of colloids in stagnant parts of a basin; it can be said that the source for silica has been the same for lydites and shungites as well.

Oversaturated orthosilicic acid (product of SiO_2 solution) polymerizes into colloid silica ($n\text{Si}(\text{OH})_4$) and then into a gel. There are two steps of gel formation: (1) condensation of $\text{Si}(\text{OH})_4$ into colloidal particles and (2) connection of the particles to aggregates. Amorphous particles of the gel are spheres with diameters up to 200 μm with the OH-groups being located on the outer surface of globules. The size of the surface area of the silica gel depends on the diameter of the particles, e. g. the specific surface of a gel changes from 68 m^2/g to 185 m^2/g when the particle diameter changes from 21 to 67 μm .

Siliceous rocks being rich in organic components (e.g. phtanites, domanikites) form as a result of the interaction between silica gel and organic matter a solution or colloid which is characterized by globules of silica covered with organic matter. For this reason these rocks are usually fine-grained.

Another source of silica becomes evident during hydromicatization of clay minerals. Clotted textures of shungite form, and the new-generated silica appears in the form of coarse-grained ideomorphic quartz filling the space between clots of organic matter.

The SEM photos showing lydites and shungites lead to the assumption that the poor crystallization of the siliceous component of the shungites is caused by the presence of organic matter. Covers in the form of films of organic matter have prevented the crystallization of silica. In case of only a little amount of organic matter the crystallization was completed fast, and organic matter formed globules between the quartz grains.

Thus, the microstructures of the siliceous component of the shungites point to a colloid nature, i. e. during the diagenesis the colloid was a friable, plastic, fluid substance preserving these features for a long time because of the adsorbed organic matter being present.

The obtained data confirm that colloid organic-silica systems can be considered a reality, and that their part in the origin of carbon-rich rocks is a very important one. Excluding the case of migrated shungites (antraxolites), all shungites forming the upper parts of deposits are metacolloid organic-mineral systems that originated from primary sedimentary sapropelic matter.

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References

- AKHMEDOV, A. M.(1995): Zakrytye metallonosnye uglerodakkumuliruyuschiy systemy volcanogenno-osadochnykh basseinov rannego proterozoya Baltiyskogo schita. (Closed metal-bearing carbon-accumulating systems of the Early Proterozoic volcano-sedimentary basins in the Baltic Shield.) - In: SCHEGLOV, A. D. (Ed.): Regionalnaya geologia i metallogeniya. (Regional Geology and Metallogeny, 4: 122-135, 6 fig., 4 tab.; Sankt-Petersburg (VSEGEI).
- ALTERMANN & SCHOPF, (1995): Microfossils from the Neoproterozoic Campbell Group, Griqualand West Sequence of the Transvaal Supergroup, and their paleoenvironmental and evolutionary implications. *Precambrian Research*, **75**: 65-90.
- 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 of hydrogenation products. - *Oil Shales*, **4** (4): 373-393, 13 fig., 4 tab.
- BUSEK, P. R., GALDOBINA, L. P., KOVALEVSKI, V. V., ROZHKOVA, N. N., VALLEY, J. W., ZAIDENBERG, A. Z. (1997): Shungites: the C-rich rocks of Karelia, Russia. - *The Canadian Mineralogist*, **35** (6): 1363-1378, 10 fig., 2 tab.
- COHEN, Y., AISENSHAT, Z., STOLER, A., JORGENSEN, B. B. (1980): The microbial geochemistry of Solar Lake, Sinai. - In: RALPH, J. B., TRUDINGER, P. A., WALTER, M. R. (Eds.): *Biogeochemistry of ancient and modern environments*: 167-172; Berlin, Heidelberg, New York (Springer).
- GERASIMENKO, L. M., ZAVARZIN, G. A. (1993): Reliktoviye cyanobakterialniye soobshchestva. (Relict cyanobacterial communities.) - In: ROZANOV, A. Y. (Ed.): *Problemy doantropogenovoy evolutsii biosfery. (Problems of Preantropogenic Evolution of Biosphere)*: 222 - 254; Moscow (Nauka).
- GLIKSON, M., LINDSAY, K., SAXBY, J. (1989): *Botryococcus* - A planktonic green alga, the source of petroleum through the ages: Transmission electron microscopical studies of oil shales and petroleum source rocks. - *Org. Geochem.*, **14**: 595-608, 13 fig., 1 tab.
- GORLOV, V. I. & BOGDANOVA, L. A. (1967): Razrabotka tehnologii i geologicheskoye izuchenie shungitovykh porod kak kompleksnogo syr'ya. (Elaboration of technology and geological investigation of shungitic rocks as complex raw material). - Report on theme **10**: 8-20, 5 fig., 2 tab.; Petrozavodsk (Institute of Geology).
- HVOROVA, I. V., DMITRIK, A. P. (1972): Mikrostrukury kremnistykh porod. (Microstructures of siliceous rocks). - 76 pp., 15 fig., 4 tab.; Moscow (Nauka).
- JUDOVICH, Y. E., KETRIS, M. P., SHULEPOVA, A. I., LAVRENKO, N. S., (1986): Geochemical diagnostic of the volcanogenic stuff in the black shales of the Lemvinsky zone of Ural. - *Geochemistry*, **10**: 1464-1476.

- KALEDA, G. A. (1987): Evolutsia kremnistogo osadkonakoplenia na kontinentalnom bloke. (Evolution of siliceous sedimentation in continental block). In: KHOLODOV, V. N. & SEDLETSKY, V. I. (Eds.): Proishozhdenie i prakticheskoe ispolzovanie kremnistykh porod. (Origin and Practical Use of Siliceous Rocks): 52-59; Moscow (Nedra).
- KALMYKOV, G. S. (1974): Svoistva metamorphizovannogo sapropelya (na primere karelskogo shungita) (Properties of metamorphosed sapropel (for example Karelian shungite)). In: VASSOEVIKH N. B. (Ed.): Problems of Oil Geology., Issue 4: 264-274, 4 fig., 2 tab.; Moscow (Nedra).
- KLUBOVA, T. T., KOROLEV, J. M., REZNIKOV, A. P. (1986): Porovoe prostranstvo i organicheskoe veshchestvo kollektorov i pokryshek. (Porous space and organic matter of collectors and covers). - 96 pp.; Moscow (Nauka).
- LANIER, W.P., (1986) Approximate growth rates of Early Proterozoic microstromatolites as deduced by biomass productivity. *Palaios*, 1, 525-542.
- MELEZHNIK, V. A., FALICK, A. E., FILIPPOV, M. M., LARSEN, O. (1999): Karelian shungite - an indication of 2.0-Ga-old metamorphosed oil-shale and generation of petroleum: geology, lithology and geochemistry. - *Earth-Science Reviews*, 47: 1-40, 21 fig., 2 tab.
- MURAVYEV, V. I. (1987): Voprosy abiogenogo osadochnogo kremnenakoplenia. (Questions on abiogenic siliceous sedimentation). - In: KHOLODOV, V. N. & SEDLETSKY, V. I. (Eds.): Proishozhdenie i prakticheskoe ispolzovanie kremnistykh porod. (Origin and Practical Use of Siliceous Rocks): 86 - 96, 4 fig.; Moscow (Nedra).
- MYCKE, B., MICHAELIS, W., DEGENS, E.T. (1987): Biomarkers in sedimentary sulfides of Precambrian age. - *Org. Geochem.*, 13 (4): 619-625, 4 fig., 1 tab.
- PHILIPPOV, M. M., GOLUBEV, A. I., MEDVEDEV, P. V. (1994): Organicheskoe veshchestvo shungitonosnykh porod Karelii. (Organic matter of shungite-bearing rocks of Karelia (genesis, evolution, methods of investigation)). - 204pp., 88 fig., 44 tab.; Petrozavodsk (Karelian Research Centre), [abstract, introduction, contents in English].
- PHILIPPOV, M. M. & ROMASHKIN, A. E. (1996): Shungitovye porody (proishozhdenie, klassifikatsia, metody opredelenia C_{org}). (Shungitic rocks (genesis, classification, methods of C_{org} determination)). - 92 pp., 17 fig., 26 tab.; Petrozavodsk (Karelian Research Centre).
- PREDOVSKY, A. A. (1970): Geohemicheskaya rekonstruktsia pervichnogo sostava metamorphizovannykh volcanogenno-osadochnykh porod dokembria. (Geochemical reconstruction of the primary composition of the metamorphosed volcano-sedimentary Precambrian rocks). - 114 pp.; Apatity (Kola Research Centre).
- ROSEN, O. M. (1970): Perestchet himicheskikh analizov sedimentogennykh krystallicheskiykh slantsev na komponenty osadochnoy porody. (Recalculation of chemical analysis data on sedimentogenical shists in sedimentary components). - *Soviet Geology.*, 7: 31-44.
- SCHOPF, J.W. (1992): The oldest fossils and what they mean. In: J.W. Schopf (Ed.): Major events in the history of life. Jones & Bartlett, Boston: 29-64.
- SOKOLOV, V. A. & KALININ, YU. K. (Eds.) (1975): Shungity Karelii i puti ih kompleksnogo ispolzovania. (Shungites of Karelia and ways of their all-purpose utilisation). - 240 pp., 34 fig., 39 tab.; Petrozavodsk (Karelian Research Centre).
- SOKOLOV, V. A., KALININ, YU. K. & DUKKIYEV, E. F. (1984): Shungity – novoe uglerodistoe syrje. (Shungites - New Carbonaceous Materials). - 184 pp.; Petrozavodsk (Karelian Research Centre).
- SOLOVOV, V. K., TUPOLEV, A. G., ZAIDENBERG, A. Z., ZVEREV, A. A. & KALININ, YU. K. (1990): Electromagnetic spectral analysis of conducting composites. - In: FRIDLANDER, I. N. & KOSTIKOV, V. I. (Eds.): MICC-90 Moscow Int. Composites Conf: 1343-1347; London (Elsevier).
- VOLKOVA, I. B. & BOGDANOVA, M. V. (1986): Petrology and genesis of Karelian shungite - high-rank coal. - *Internat. J. Coal Geol.*, 6: 369-379, 3 fig., 1 tab.
- ZHMUR, S. I., GORLENKO, V. M., ROZANOV, A.YU. (1993): Cyanobacterial system - a producer of organic matter for shungites of Karelian Lower Proterozoic. - *Lithology and Mineral Resources*, 2: 122-127, 3 fig.

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Sample component	1	2	5	6	7	9	10	11, 11A, 12, 14, 15
SiO ₂	54.78	47.18	23.73	17.58	0.7	0.26	6.07	n.d.
TiO ₂	0.21	0.26	0.49	0.22	0.04	<0.01	0.11	n.d.
Al ₂ O ₃	3.67	4.32	4.26	4.5	0.2	0.52	0.72	n.d.
Fe ₂ O ₃	1.25	0.94	2.55	3.42	0.5	1.02	0.13	n.d.
FeO	0.54	0.36	0.3	n.d.	-	n.d.	0.36	n.d.
MnO	0.02	0.013	0.006	0.022	-	0.015	0.009	n.d.
MgO	0.26	0.26	0.72	1.72	1	<0.01	0.53	n.d.
CaO	<0.01	<0.01	0.07	0.42	n.d.	0.28	0.14	n.d.
Na ₂ O	0.03	0.05	1.37	0.2	0.05	<0.01	0.14	n.d.
K ₂ O	0.81	0.8	1.54	1.52	0.04	0.02	0.19	n.d.
H ₂ O	0.5	0.36	2.91	0.7	2.54	1.68	1.6	n.d.
LOI	37.36	44.92	64.23	70.27	95.36	98.03	91.38	n.d.
P ₂ O ₅	0.02	0.04	-	-	-	-	0.04	n.d.
Cr ₂ O ₃	0.016	0.013	0.021	-	0.007	-	0.005	n.d.
V ₂ O ₅	0.031	0.034	0.503	-	0.12	-	0.068	n.d.
CoO	<0.001	<0.001	<0.005	<0.005	-	<0.005	<0.001	n.d.
NiO	0.004	0.006	0.025	0.016	-	0.011	0.051	n.d.
CuO	0.005	0.003	0.009	0.008	-	0.028	<0.001	n.d.
ZnO	0.001	0.002	0.02	0.007	-	0.005	0.003	n.d.
Li ₂ O	-	-	0.0014	-	-	-	-	n.d.
Rb ₂ O	-	-	0.0022	-	-	-	-	n.d.
Cs ₂ O	-	-	0.0002	-	-	-	-	n.d.

Table 1. Chemical composition of shungite rocks and shungite from Onego Lake area, Russian Karelia (in %). 1, 2 - shungite rock III, Maksovo; 5 - shungite rock II, Maksovo; 6 - shungite rock II, Shunga; 7 - layer-shungite I, Shunga; 8 - shungite rock III (sooty), Maksovo; 9 - vein-shungite I, Maksovo; 10 - vein-shungite I, Chebolaksha; 11 - shungite from anthraxolite "pancake" structure in Kalevian siltstones; 11A - host rock (carbon-bearing siltstone); 12 - shungite rock IV, Maksovo; 14 - shungite rock IV (sooty), Pazha; 15 - shungite rock III, Pazha.

TABLE (continued)

Sample nn	1	2	5	6	7	8	9	10	11	11A	12	14	15
C _{tot} %	39.95	41.70	56.40	62.00	90.00	15.00	86.00	68.10	35.20	3.60	6.10	20.40	32.20
C _{org} %	39.40	41.20	56.20	61.50	88.50	14.50	84.50	67.90	32.20	3.30	5.60	20.00	31.70
S _{tot} %	0.400	0.705	2.05	5.300	0.440	0.280	0.240	0.330	0.090	0.040	0.770	0.180	0.280
S _{HCl sol.} %	0.315	0.530	1.55	4.900	0.420	0.250	0.230	0.320	0.080	0.030	0.705	0.150	0.200
As	30	<10	190	220	140	<10	15	<10	<10	<10	<10	<10	<10
Ba	345	425	180	106	5	680	9	102	80	205	590	1500	1450
Co	3	7	24	45	21	13	2	4	23	70	19	15	6
Cr	65	66	111	60	5	86	7	42	35	140	800	72	82
Cu	19	16	68	57	66	7	142	17	640	280	90	40	36
Mn	16	28	8	22	23	132	10	27	1220	820	450	110	42
Mo	16	13	295	208	192	12	<5	<5	<5	<5	<5	15	19
Ni	204	375	400	300	1170	82	130	335	555	265	130	39	42
PO ₄	300	130	200	250	190	900	260	<100	550	1050	800	<100	100
Sb	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
Ti	1450	1690	2310	1705	27	7840	18	440	1050	1880	4050	3500	3740
V	150	165	1480	800	800	210	53	300	180	300	410	210	225
Zn	8	25	145	45	233	185	15	70	65	95	125	48	27

LOI = loss on ignition. n. d. = not determined. (-) = below detection limit. Determination of rock-forming oxides was done by wet chemistry at the Institute of Geology in Petrozavodsk. Determination of total carbon (C_{tot}), organic carbon (C_{org}) and total sulfur (S_{tot}) were done by combustion analysis with infrared detection using LECOMAT CS 244. For determination of trace elements samples were burned at 750° C for 1/2 hour. The concentrations of the trace elements are related to these dry ash residues (Concentration in ppm).

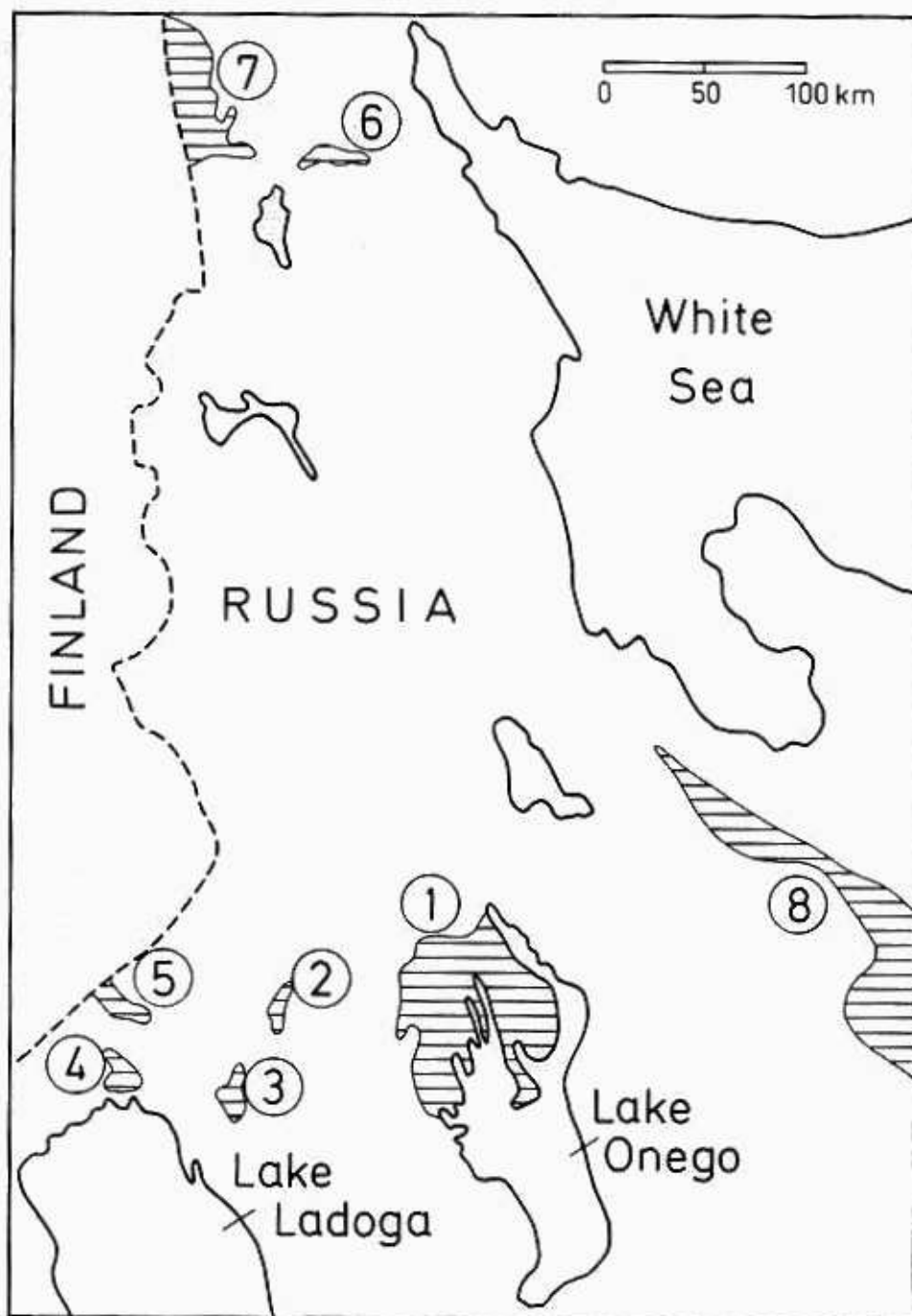


Fig. 1. Deposits of Paleoproterozoic carbon-rich rocks in Karelia. Geological structures: 1 = Onego, 2 = Suojarvi, 3 = Tulomozero, 4 = Kirjavolahti, 5 = Janijarvi, 6 = Kukasozero, 7 = Pana-Kuolajarvi, 8 = Windy Belt.

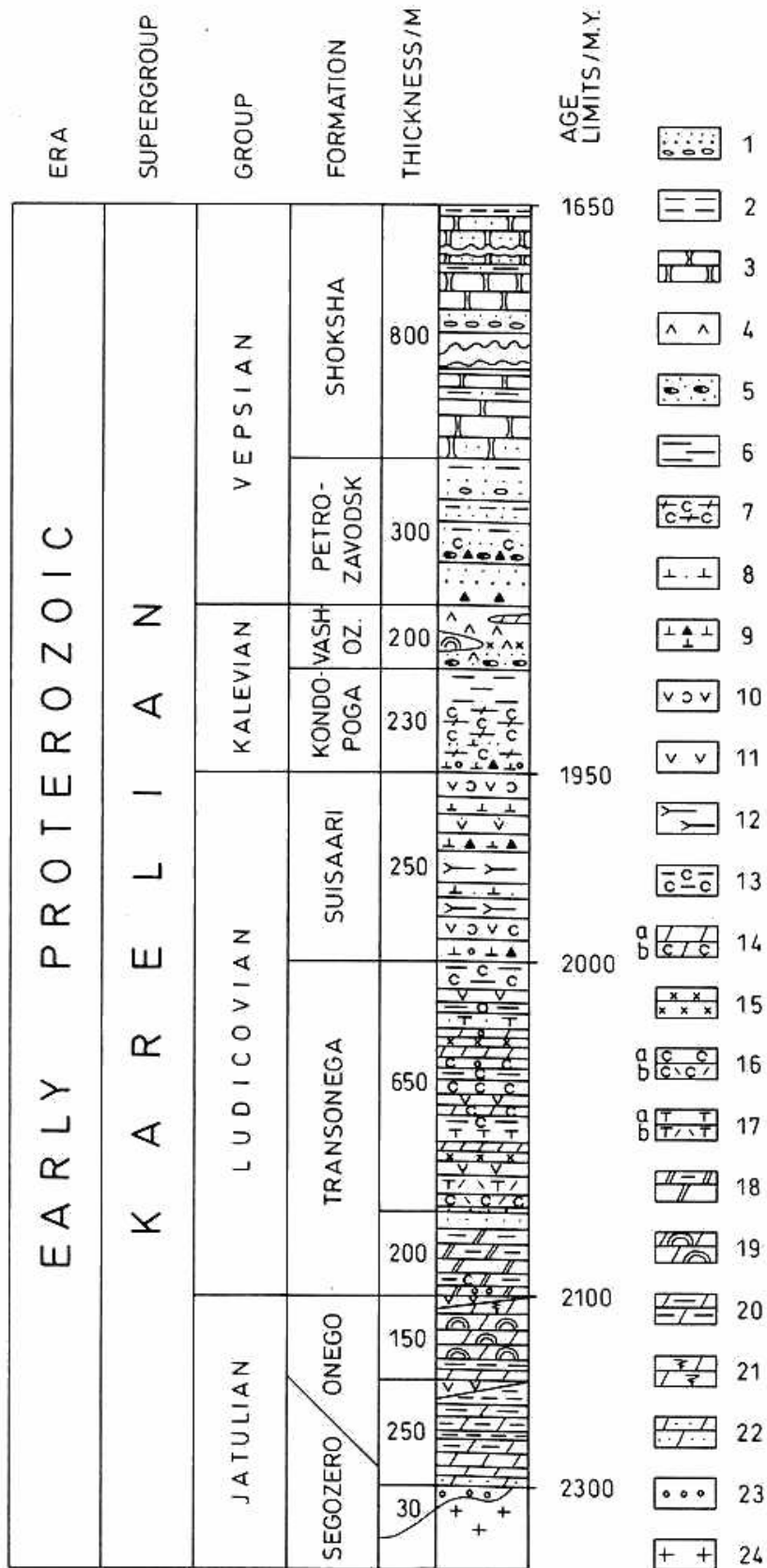


Fig. 2. Stratigraphic sequence of Paleoproterozoic Onego structure (Onegian synclinorium).

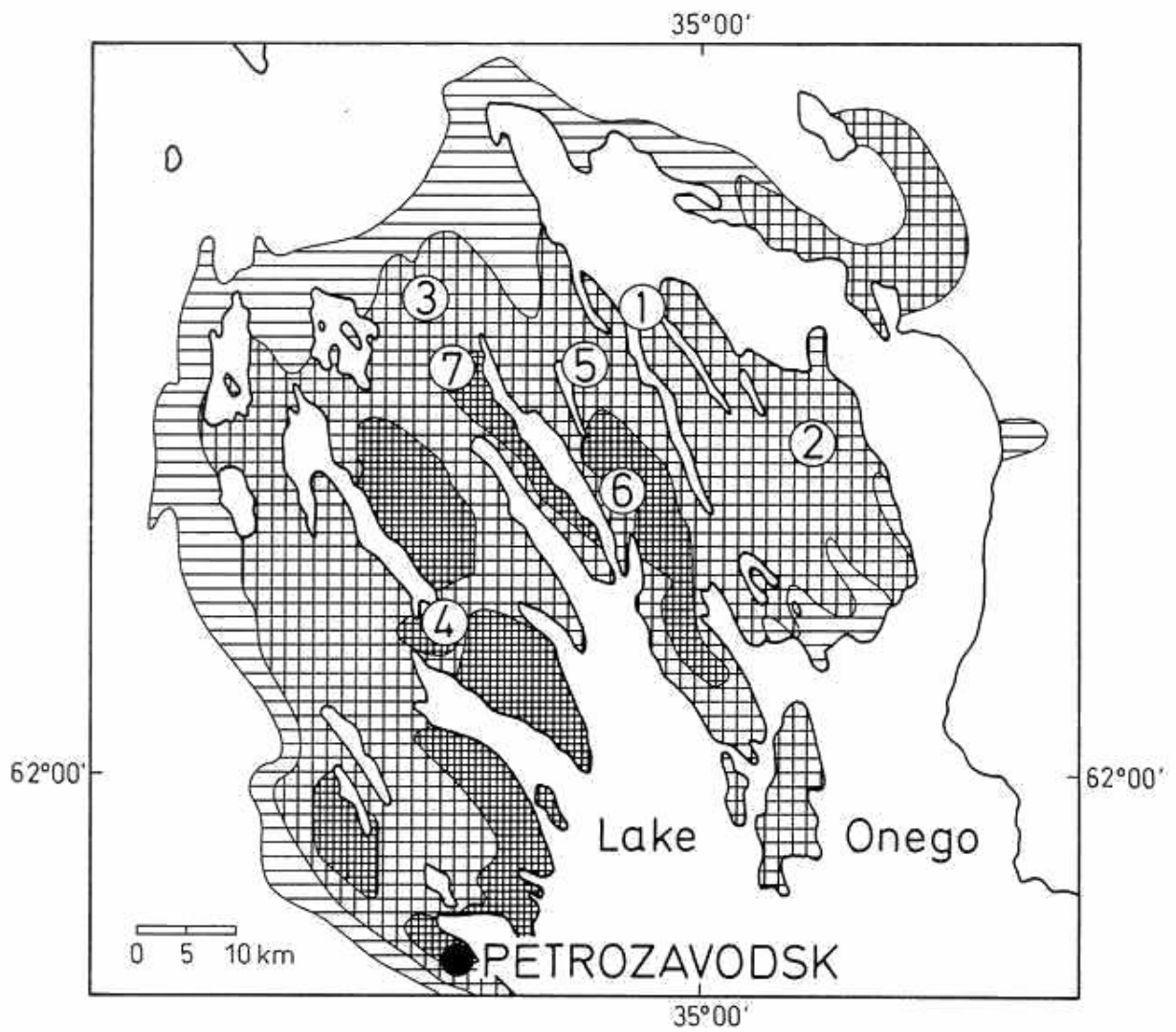


Fig. 3. Onegian synclinorium showing the Lower Proterozoic stratigraphic units: x - Jatulian, xx - Ludicovian, xxx - Kalevian and the shungite deposits: 1 = Shunga, 2 = Maksovo-Zazhogino, 3 = Kyappeselga, 4 = Nigozero, 5 = Myagzero, 6 = Krasnaya Selga, 7 = Vikshozero.

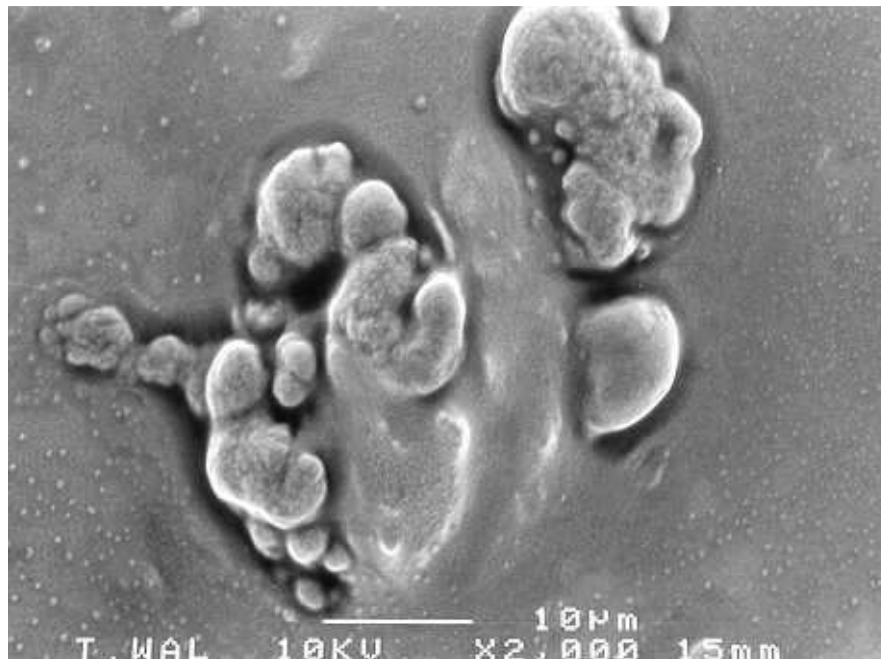


Fig. 4. Microtexture of lydites from the Shunga deposit. Metacolloform-globular structure. Bar is 10 µm. White = carbon, black = pores and cracks, grey = silica.

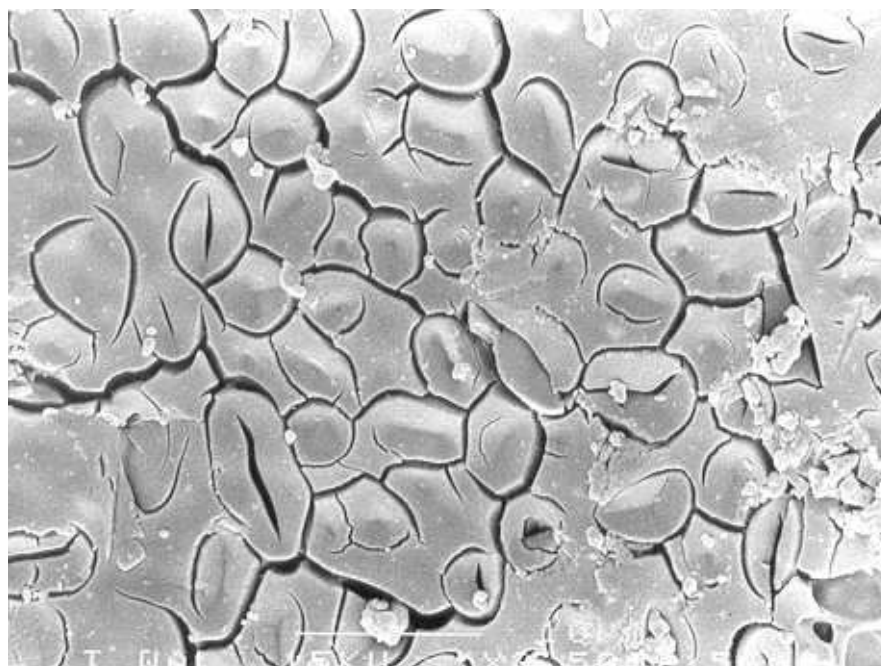


Fig. 5. Microtexture of lydites from the Shunga deposit. Metacolloform structure with dehydration cracks of organic-silica gel. Bar is 10 µm. White colour= carbon, black = pores and cracks, grey = silica.