Organic matter of sediments of South Chukotka

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Abstract. The article discusses data on paleosol, mineralogy, and paleobotany obtained as a result of studying material collected from the Maastricht-Early Paleocene sediments of the Tanyurer Formation of South Chukotka. The burial of organic matter in the sedimentary rock of the Tanyurer Formation is associated with deflationary processes during the period of activation of volcanic activity. On the drained volcanic plateau of soil formation, a sod humus-accumulative process prevailed under the steppe vegetation. Humic substance dispersed in sedimentary rock was represented by a group of humins resistant to microbial decomposition. As a result of exposure to high pressures and temperatures, the colloidal form of humus was transformed into kerogen. Organic compounds (cellulose, lignin) in the plant tissue of buried tree trunks were replaced by silicon compounds. Weathering processes have affected the thin surface layer of dense sedimentary rock. Under the influence of the temperature and humidity gradient, loosening of loose rock and disintegration of clots of colloidal forms of humus occurred.

1 Introduction

The remains of the fossil forest were found in the bay of the Anadyr estuary south and east from Cape Dionysius [1, 2]. In total, two locations were discovered with vertically standing trunks of fossil trees overlain by volcanic sedimentary deposits of the Tanyurer Formation, which dates from the Late Maastricht - Early Paleocene [1, 3, 4]. This is the only find of petrified trees in the Arctic, buried in places of their original growth in sedimentary deposits. During field excavations of the remains of the buried forest in the east of Cape Dionysius at the foot of the slope, loose formations similar to buried soils [2] were discovered. A paired study of petrified trees and paleosols opens up the possibility of reconstructing the paleoecological conditions for the growth of the Temlyan flora of South Chukotka [3]. The objects of research are petrified wood and dispersed organic matter (OM) in hard and loose mineral deposits in which forest vegetation is buried.

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The remains of a vertically standing petrified tree trunk, available for research, were found east of Cape Dionysius in the lower part of a steep slope facing the estuary. The slope is a rock outcrop with a height of about 20 m, consisting of two layers. The lower layer is composed of a dense cemented gray rock, covered with a thin (3-5 cm) case of loose, viscous, clay mass. It is covered by a 4-meter thick dark brown basalt.

The trunk of the buried tree is at the junction of cemented gray and loose black rock. The latter is a separate body in the enclosing gray rock. Judging by the shape and size, the black rock fills the erosion hollow of the drain, overlapped by gray rock. Both breeds are similar in texture and mineralogical composition. They are composed mainly of feldspars and quartz. Secondary minerals are represented by mica, clay minerals and iron oxides. A paired study of petrified trees and paleosols opens up the possibility of reconstructing the paleoecological conditions for the growth of the Temlyan flora of South Chukotka [3].

2 Materials and methods

The objects of research are petrified wood and dispersed organic matter (OM) in hard and loose mineral deposits in which forest vegetation is buried. Petrified wood is a remnant material from distant epochs that was fossilized in a mineralized form [5]. Samples of loose black rock at different depths of the section were selected, as well as samples of hard and loose rock of black and gray colors, fragments of a petrified tree branch to conduct analytical studies of the composition and properties. Thin sections were made of all these elected samples. The study of the structure, mineralogical, and chemical composition of the samples was carried out using classical optical microscopy, as well as electron microscopy with microprobe analysis. Micromineralogical studies were carried out on the equipment of the resource center «Microscopy and Microanalysis» (St. Petersburg State University Science Park). Petrographic preparations (thin sections and polished sections) were made from undisturbed and non-oriented large aggregates of samples. Sections of petrified wood were made across the tracheid.

3 Results and discussions

In samples of hard rock of black and gray colors, OM is present in the form of inclusions (“grains”) of various shapes and sizes, scattered among the mineral mass from primary and secondary minerals. There are very few direct contacts of primary minerals and OM grains. Grains of organic matter at a small increase (x2.5) stand out in black and have a uniform texture. As a rule, grains are surrounded by a finely dispersed material acting as cement.

With a tenfold increase in large OM grains in black rock, three types of OM structure are revealed:

1. Homogeneous;
2. Motley, i) with a high content of small grains of minerals, but with a predominance of black OM; ii) with the predominance of small grains and black clumps of OM, forming a mesh pattern (Fig. 1a);
3. Spotted (black spots of different sizes and with diffuse borders stand out against a dark gray background).

The combination of large black OM grains and primary minerals creates a very contrasting color pattern (Fig. 1b). Coarse mineral grains often have a very thin film of dark color. Due to the black film of organic matter covering mineral grains, the rock is black in color. The number of OM grains in the gray rock is much smaller than in black. It is dominated by small, mixed-grained OM inclusions having an irregular angular shape. Large grains that are rounded in shape are rare and they are much smaller than in black rock (BR).

Large grains of OM are immersed in clay cement, and small grains are more often dispersed in a fine-grained mass. In general, OM is dispersed unevenly in the rock mass. Plots with a high content of different-grained OM are distinguished in places. Figure 1a shows the heterogeneity of the rock, consisting of well-isolated areas that differ in structure, degree of dispersion, and grain size. In gray rock (GR), the same OM structures are present as in the GR. Several isolated fragments with an unusual pattern texture were revealed. One fragment is represented by a transverse section of a petrified plant stem (Fig. 1c); a series of concentric formations, possibly the walls of the vascular system of plants, are clearly visible on the section.

Loose rock samples have a loamy granulometric composition. The carbon content of organic compounds (Corg.) in the fine-grained BR varies from 0.16 to 0.35%, and in the gray rock Corg. is not found. In the mud fraction, the amount of Corg in the samples, GR was 0.46%, and in samples from BR 0.98%. A peculiarity of loose rock is a highly alkaline reaction of water extract (8.5-9.1). At the same time, the rock did not boil during treatment with 10% HCl. The high loss on ignition in all samples is associated with the features of the mineralogical composition. In thin sections, the distribution structure of OM in loose black and gray rocks differs significantly from the dense one. Large forms of OM are mostly disintegrated and more evenly distributed over the entire area. In light rock, the size of the contours is smaller than in black. Their shape is predominantly elongated and has a jet structure; the borders are rugged, often scalloped. In both samples, rare large grains of OM were preserved. When zoomed in, they look like flakes.

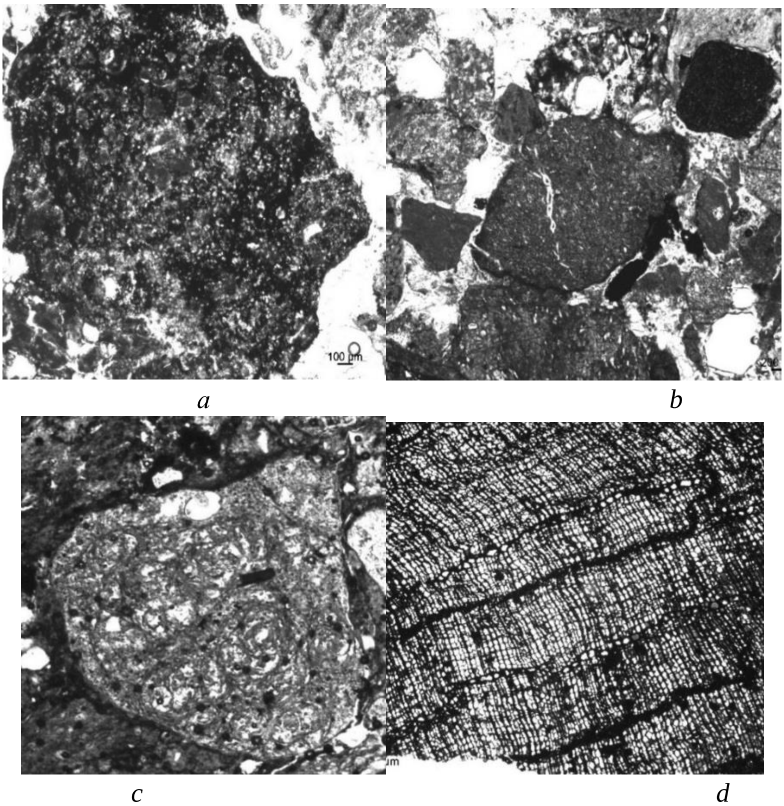

Fig. 1. The structure of organic matter on petrographic sections (explanation in the text).

The study of organic matter of the thin section of the petrified branch revealed a high preservation of the cell structure with the complete replacement of plant tissue with quartz minerals. OM in petrified wood was partially preserved only in the intercellular walls (Fig. 1d).

A good proof of the mechanical disintegration of large OM grains in black loose rock is the accumulation of homogeneous black clumps. Their shape and boundaries are well mated with each other (Fig. 2). The number of OM clots in an emergency is noticeably greater than in a gray one. A characteristic feature of the studied thin section is the high content of thromboid pyrite (Fig. 3).

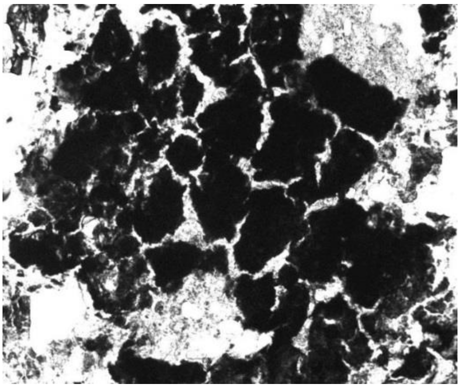

Fig. 2. Fragments of a large grain of organic matter in loose black rock.

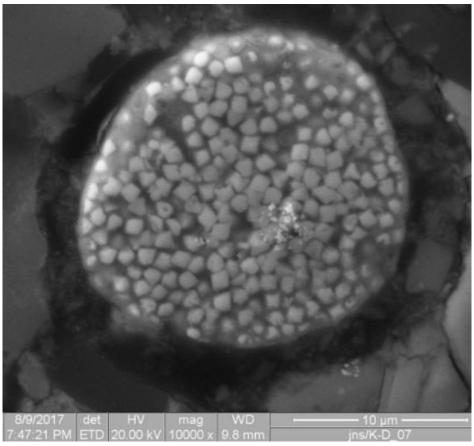

Fig. 3. Thromboid pyritein petrified wood.

OM in solid rocks is mainly in the dispersed state in the form of morphologically isolated grains having different size, shape, structure and nature of the boundaries. Grains are a mixture of humus-like OM with minerals of varying degrees of dispersion. In loose rock, OM is mainly flaky. The state of organic matter in hard and loose rock distinguishes it from primary and secondary minerals. Rare inclusions in the rock of plant fragments that partially retained the shape and structure of plant tissues were found only in loose gray rock.

The nature of OM dispersed in solid rock is not clear. It is known that OM interspersed in the mineral mass in sedimentary rocks belongs to kerogens. At present, kerogen is often used to indicate syngenetic disseminated OM of any genetic type. Kerogen is an OM insoluble in organic solvents. It is a spherical colloidal particle with a diameter of 20-140 microns. It is formed from organic matter of different genesis under the influence of high pressure and temperature [6]. The chemical structure of kerogens is determined mainly by the state of the initial OM and the chemistry of its transformation in diagenesis. The low permeability of kerogen governs the storage and production of shale gas. The flexible kerogen constantly experiences mechanical deformation induced by reservoir environment and complex interplay with geofluids [7]. Currently, there are three main mechanisms of conservation of OM in the [6] rock. The first mechanism is associated with degradation processes — the decomposition of biogenic polymers and the “random” condensation of their decomposition products into a new polymer, kerogen. This type of kerogen is formed from algal lipids or lipid-rich OM. The second mechanism is “natural vulcanization” of OM of marine origin. The third mechanism for the conservation of OM in sediment is called “selective conservation”. It is associated with the residual accumulation of organic molecules that are most resistant to diagenesis factors during the destruction of less stable ones. This type of kerogen is formed from the decomposed residues of higher terrestrial plants [6].

Kerogen of the third type includes mainly condensed polyaromatic or oxygen containing functional groups (aliphatic units play an insignificant role). Kerogen of the third type has a low H / C ratio (less than 1.0) and a high O / C ratio (0.2-0.3). As a rule, decomposition of organic residues occurs in subaerial river conditions. Their microbial decomposition is impeded by the high rate of sediment accumulation and their rapid burial in the sedimentary strata of the continental margins [8]. The lack of data on the chemical composition of organic matter in the samples under study does not allow a direct method to determine its initial state and, thus, the type of kerogen. However, an analysis of the conditions for the formation of sedimentary deposits and the mechanism of their formation opens up this possibility.

The territory of South Chukotka in the Late Cretaceous - Early Paleocene was not homogenous in landscape terms. In addition to volcanoes, as well as volcanic plateaus, there were coastal lowlands, foothill valleys and hollows that inhabited [1] woody plants. The data obtained from thin sections of wood from Cape Dionysius [1] make it possible to classify the studied wood as gammamelid or plane tree, as well as cypress and pine. It was probably a floodplain coniferous-deciduous forest dominated by conifers. The buried forest occupied the periphery of the river delta, turning into a steep slope of the volcanic plateau.

Filling the delta with sedimentary material and burying trees was a one-time process. The forest was probably buried as a result of aeolian transfer of fine earth in the direction from the volcano to the river delta. This hypothesis is supported by the size of sedimentary particles (less than 2 mm) and the presence of dispersed organic matter mainly in colloidal form, as well as very rare inclusions of small weakly decomposed organic residues, lack of roundness of mineral grains and vertical arrangement of trunks that have preserved side branches.

Judging by the nature of the organic residues on the drained plateau in the soils, a sod-humus-accumulative process prevailed, developing under grassy vegetation. The development of arboreal and shrubby vegetation could be hindered by increased gas contamination of the atmosphere near the territory of active volcanoes, a high content of toxic compounds (the possibility of acid rain). The outgrowths on the outer parts of the branches and trunks of fossil trees in the form of burls indicate a strong gas contamination of the atmosphere. The growths are located on the outside of the branches, which reach 2-15 cm in diameter. The growths were formed as a result of a change in cambium growth caused by the gas contamination of the atmosphere due to nearby volcanoes.

The formation of loose sediment in the river delta occurred in two phases. In the first phase, the forest was buried by aeolian sediment. The second phase is associated with water erosion caused by liquid precipitation. As a result of the redistribution of surface runoff onto a plateau, elementary drainage basins and an erosion-brook network were formed [9]. It received soil material brought with surface runoff from the catchment area.

The fine-grained, water-erosive material accumulated over a large area was compared to deflationary material and was more enriched in organic matter and large fractions of fine earth. Another distinctive feature of it was the large roundness of the grains and their round shape. This is confirmed by a comparative analysis of the morphological structure in thin sections of black and gray hard rocks.

Water-erosive material was transported along the hollows of the runoff in friable gray rock to the foot of the slope, local loose clusters with a characteristic black color due to humic substances formed. Humic substances covering the surface of sand particles, together with organomineral (humus-clay) aggregates, caused the black color of water-erosive material. (Such an erosion hollow, filled with black material, was opened by a laid cut.) Judging by the size and shape of the erosion hollows, the precipitation was not long. After their cessation, water-erosive material was buried under aeolian sediment.

The formation of loose precipitation, which covered the trees, ended in connection with the activation of the volcano and the eruption of lava. Basaltic lava blocked the loose sediment that covered the forest, and the access of oxygen and water to them. The transformation of dispersed organic matter, as well as OM in the wood trunks took place under conditions of high temperatures and pressure, with a progressive loss of capillary and then physically adsorbed moisture at the beginning.

The nature of the change in the buried OM of sedimentary rocks in colloidal form was fundamentally different than in buried wood trunks. The dispersed OM was in the deposits in the form of humus-clay complexes and aggregates with finely dispersed minerals. The OM of the buried wood was represented by plant tissue, consisting mainly of cellulose and lignin. It is known that the main mechanism of OM transformation is microbial decomposition. In the wood of the trunk due to the preservation of the water supply system for a long time, the movement of solutions could be carried out. Gradients of temperature, pressure, humidity, and concentration of soil solution at the boundary between the trunk and sedimentary rock were the mechanism of chemical compounds entering the trunk. As a result of the gradients, water with silicon compounds dissolved in it could flow from the rock into the trunk. This process could continue until the complete loss of capillary and then film moisture.

Intracellular organic matter, represented by cellulose, as less resistant to microbial degradation, was primarily destroyed. Released voids filled siliceous solutions. The well-known process of replacing plant tissue with silicon (opal, chalcedony) followed by the formation of quartz. The entry of silica into the tree trunk through the pores was facilitated by a difference in reaction (acidic in the wood and alkaline in the surrounding sediment). An acidic reaction inside the trunk was created due to the destruction of plant tissue by microorganisms, during which carbon dioxide was formed. The decomposition of the cell membrane, consisting of lignin, and their replacement with silicon, occurred in the second place, which helped to preserve the structure of plant tissues. The process of transformation of organic matter in the trunk ended in complete petrification. According to published data [8, 10, 11], intracellular substitution of OM occurs under conditions of burial at high water content. Usually, this occurs during sedimentation in a wide range of facies from marine to continental, most often in river deltas, channels, and coastal marine areas. In our case, there is no evidence of excess water in sedimentary rock. The conditions and sedimentation mechanism under which the forest was buried were different.

Changes in OM dispersed in the rock were less significant. The initial humic substances sorbed by clay minerals are highly resistant to microbial decomposition. First of all, this concerns humins (non-hydrolyzable part of humic substances of the soil). Their share in the group composition of humus can reach significant values (70% or more). Under buried conditions, the separation of humic substances under the influence of microorganisms could increase. The fractions of FA and HA less resistant to microbial decomposition were mineralized with residual accumulation of a stable fraction (humins). Loss of moisture, probably high temperature, led to the transformation of humins and their transformation into third-form kerogen. Organic matter as a result acquired a solid consistency, as well as clay rock. The process of converting dispersed humic substances to kerogen and silicification of plant wood tissue ended as a result of the loss of free and physically adsorbed moisture, as well as re-compaction.

The current stage of transformation of sedimentary deposits is associated with processes of predominantly physical weathering in the surface layer of the rock in contact with the atmosphere. Gradients of temperature and humidity are the main factor in the transformation of surface dense rocks into loose. Petrified wood was not affected by weathering processes. Significant changes in the dispersed OM in the weathering layer were manifested, first of all, in a change in its consistency and shape. As for the structure, there were no significant changes in it. An attempt to isolate humic acids by the method of Tyurin failed. This suggests that humins predominate in OM. In addition to the bond strength with clay minerals, the resistance of OM to microbial action is facilitated by the alkaline reaction of the soil solution.

4 Conclusion

The burial of OM in the sedimentary rock of the Tanyurer Formation is associated with deflationary processes during the period of activation of volcanic activity. On a drained volcanic plateau, a soddy humus-accumulative process of soil formation under the steppe vegetation predominated. Humic matter dispersed in sedimentary rock was represented by a group of mainly humins resistant to microbial decomposition. As a result of exposure to high pressures and temperatures, the colloidal form of humus was transformed into kerogen. Organic compounds (cellulose, lignin) in the plant tissue of buried tree trunks were replaced by silicon compounds. Weathering processes affected the thin surface layer of dense sedimentary rock. Under the influence of the temperature and humidity gradient, loosening of loose rock and disintegration of clots of colloidal forms of humus occurred.

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