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Mineralogical and lithological properties of Domanikites from the south-east of Tatarstan Republic

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Abstract. The article was described main types of rocks – mudstones, carbonate-siliceous rocks, containing organic matter and carbonate breccia, based on detailed analysis of rock samples from Semiluksky horizons of Upper Devonian black shale formations, Volga-Ural region, Russian Federation. Different structures and texture features, mineral composition, and content of organic matter characterized selected types of rocks. Only in the carbonate-siliceous type of rocks is the high content of organic matter, about 9%. It was found direct dependence between the content organic matter and content in rocks silica minerals (quartz and chalcedony). Such dependence caused by joint precipitation silica minerals and accumulation of organic matter in the seafloor in conditions of active seepage of hydrothermal fluids. The presence of an abundance of biophilic elements in ascending fluids led to an explosion of biota and widespread of silica organisms. This hypothesis doesn't disagree with any authors but considers the significant contribution of fluid factor to the deposition of Semiluksky formations.

1. Introduction

Reserves of traditional sources of energy and paces of exploitation of hydrocarbon reservoirs are both limited. More attention gets the exploitation of new hydrocarbon resources. According to various estimates, the reserves of unconventional oil sources are five times higher than traditional reserves [1]. Exploration of unconventional hydrocarbons can be highly profitable and the share of unconventional oil is increasing from year to year in the world. Oil and gas fields in shale formations are the unconventional hydrocarbon deposits. The "shale revolution" in the USA made the country of the world's leader in oil production overtaking Russia and Saudi Arabia [2]. Many companies and researchers focus on carbonate-siliceous rocks of Semiluksky horizons, named also domanicites, as unconventional oil reservoirs [3, 4, 5, 6].

In the Upper Devonian carbonate-siliceous rocks of the Semiluksky horizon is observed high content of organic matter [7]. According to the results of vitrinite and pyrolytic analyzes [3, 8], the organic matter has a low maturity (Protocatageneez-Mesocatagenez). Such catagenetic gradations indicate the stage of the beginning of the oil window and the beginning of hydrocarbon generation. Carbonate-siliceous rocks of the Semiluksky horizon have only partially exhausted their hydrocarbon potential, based on the

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provisions of the sedimentary-migration theory of the formation of oil and gas fields [9]. It indicates the prospect of exploitation such as rocks in the future. An important aspect of the study of such strata is the determination of their lithological characteristics and composition of organic matter. This is necessary for future exploration and the selection of optimal schemes of exploitation for such deposits.

The main purpose of the paper is an investigation of the mineral and lithological composition of rocks and the composition of organic matter. Samples were selected from Upper Devonian carbonate-siliceous black shale formations from the Tavelskoye oil field, the eastern side of the Melekesskaya depression of the Volga-Ural anticline, the east of the Russian platform. The Interval of depths was 1777.0-1799.0 m.

2. Methods

On the first stage authors have done detailed macroscopic description of the core samples. According to the description, the main lithotypes were identified. For every lithotype were determined mineral composition and composition of organic matter. Next stage was a petrographic description of thin sections. For studying authors used polarization microscope "Axio Imager A2". In addition, the method of x-ray diffraction was used for detecting of the total mineral composition of the rocks and minor minerals. For analysis was used D2 Phaser diffractometer and DIFFRAC.EVA and TOPAS software. For qualitative characteristics of organic matter we used the method of synchronous thermal analysis based on the STA 443 F3 Jupiter, Netzsch. The method at a qualitative level made it possible to establish the proportion of light and heavy hydrocarbons in the studied rocks, as well as the presence of kerogen.

3. Results and discussion

Lithotype is type of rock identified mainly by lithogenetic characteristics of rocks and features that is reflect the conditions of its formation [10]. According to a detailed description of the core were divided three lithotypes, based on an analysis of the mineral composition, structural and textural characteristics of the rocks, as well as the organic matter content.

Mudstones (Fig. 1B) in the samples are represented by gray and dark gray fine grained limestones, with rare calcite veins up to 0.5 cm, located perpendicularly, less often parallel to layering. The rocks are characterized by unregularly spotted oil saturation. According to petrography, grains are represented by rare fragments of algae and make up 3-5% of the total rock volume. The rocks are dense, pore space is not detected (Fig. 2A).

Carbonate-siliceous rocks (Fig. 1C) are gray and dark gray. Visually, the rocks are characterized by a dense and fine grained structure. Gray and dark gray color is due to the presence of organic matter. Often in the rocks, the presence of subhorizontal, less often subvertical veins filled by calcite with a thickness up to 3 mm. Limestone concretion are sometimes noted in rocks and characterized by light color and free of organic matter. According to petrography, the rock structure is fine-grained, microtexture is layered. Calcite grains often form a dense structural packing. Quartz, which makes up 40% of the rock, forms small, fine-grained aggregates; in parts, it forms fibrous aggregates. The fossils have bad preservation due to recrystallization processes. The rocks are dense; porosity was not detected under optical microscopy (Fig. 2C).



В







Mudstone



Carbonate Breccia

Figure 1. An example of a section of and samples. A - Studied section, core material. Lithotypes: B - Mudstone, C - Carbonate-siliceous rocks containing OM, D - Carbonate breccia.

Breccia in the studied section are rare and do not form units of any significant thickness. So fragments usually have a carbonate composition. The fragments are often angular in shape and have an unregular position in rocks (Fig. 1D) and are represented by fragments of mudstones. Cement is a carbonate-siliceous material with dispersed organic matter.

Petrographic studies revealed some types of diagenetic transformation of rocks. Secondary dolomitization is often observed in the carbonate-siliceous rock, confined to the development of stylolites. Crystalls have an idiomorphic and hypidiomorphic structure (Fig. 2E). According to x-ray data, the mineral composition was detailed. Thus, by the mineral composition. Mudstone consists of 90% from calcite and 10% from quartz. Carbonate-siliceous consists of 40% from quartz, on 48% from calcite, on 8% from mica, on 4% from microcline. Breccia consists of 61% from calcite, on 16% from quartz, on 10% from mica, on 2% from dolomite (Table 1).



Figure2. Photo of thin sections of studied lithotypes. A –mudstone normal light (NL), B – mudstone polarizer light (PL), C – carbonate-siliceous rocks NL, D –carbonate-siliceous rocks PL, E – secondary dolomitization NL, F – secondary dolomitization PL.

Table 1. Table of mineral composition of selected lithotypes								
	Calcite, syn	Quartz, syn	Mica	Microcline	Dolomite	Piryte		
Lithotype 1	91%	9%	-	-	-	<1%		
Lithotype 2	48%	39%	8%	4%	-	<1%		
Lithotype 3	61%	16%	9%	_	2%	<1%		

The organic matter of the rocks was investigated by the method of thermal analysis (Fig. 3). In carbonate-siliceous rocks contain light hydrocarbons (LUV), heavy hydrocarbons (TUV), kerogen is sporadically detected. The results of the analysis are presented in table 2.



Figure 3. TG and DTA curves of carbonate siliceous rocks.

Lithotype		The content of organic matter, weight, %	Content of organic		
			matter, %		,)
			light hydroca rbons	heavy hydroc arbons	Kerogen
Lithotype 1 Mudstone		Absent		Absent	
Lithotype 2 Carbonate-siliceous rock		9,3	31	63	0-6
Lithotype 3 Breccia	Clasts	Absent		Absent	
Diccolu	Cement	8,73	57	43	0

Table 2. The average content of organic matter in carbonate-siliceous rocks

In the section, carbonate and carbonate-siliceous rocks form interbedded bodies and rarely form independent units (Fig. 4). Carbonate breccias are extremely rare in the section. Thin lamination of lithotypes indicates the cyclical formation of deposits. An idealized section consists of alternating carbonate and carbonate-siliceous rocks saturated with organic matter.



Figure 4. Scheme of precipitation siliceous and carbonate minerals

Carbonate breccias are a result of the gravitational transfer of carbonate material and the alternation of carbonate and carbonate-siliceous rocks is explained by various sources of material input into the seafloor.

The study of carbonate-siliceous strata of the Semiluksky (Domanic) horizon of the Upper Devonian showed that the deposition of strata was in the deep part of the shelf, below the wave base level. At the same time, the accumulation was a joint of organic matter and siliceous minerals (fig. 5). This is indicated by a direct relationship between the content of organic matter and the number of siliceous minerals (quartz and chalcedony). It appears that these components are genetically related. The data indicates the silica introduced to the basin as a result of the discharge of hydrothermal or heated fluids. The components of fluids led to widespread of the silica organisms and deposition in stagnant bottom environments with siliceous minerals.



Figure 5. Cross-plot diaframm of the content of quartz and organic matter in carbonate-siliceous rocks.

4. Conclusions

1. Three main lithotypes are distinguished in the Semiluksky (Domanik) horizon: carbonate rocks, carbonate-siliceous rocks, breccias.

2. Syngenetic organic matter was found in carbonate-siliceous rocks with a content of up to 9%. Organic matter is predominantly heavy hydrocarbons, lesser light hydrocarbon and kerogen.

3. The dependence of the amount of siliceous minerals and organic matter is associated with the silica fluids and silica organisms. On the one side, fluids stimulate the growth of siliceous organisms; on the other side, the abundance of biophilic elements in fluids stimulates the extensive widespread of biota and accumulation of organic matter.

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