Secondary dolomitization of the Domanik black shales as an indicator of gas-water hydrocarbon-containing fluids upward migration in the Tatarstan territory

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Abstract. The share of unconventional oil reserves is high in Russia and Volga-Ural region, including shale oil reservoirs. It contains around 65% of the total volume of hydrocarbon reserves in region, according to various data. Shale hydrocarbons are widely used in Russia. The main part of the Domanik black shale is confined to carbonate-siliceous carbonaceous complexes of the Domanik horizon of the Francian stage of the Upper Devonian system. According to previous studies in the Domanik formation sedimentary complexes of the Volga-Ural oil and gas province, two types of rocks are distinguished - the Domanikites themselves and Domanikoids. Domanikites contain from 5 to 20% organic matter. Both types of carbonaceous rocks have a practically similar lithological composition. The difference between them lies in variations in siliceous component content and number of authigenic minerals. If content of very fine-grained silica was determined by primary sedimentation factors, then authigenic minerals are indicators of secondary lithogenesis processes. In this work, an attempt is made to compare organic matter content with dolomite mineralization, which is an active agent in mineral formation.

1. Introduction

In recent years, in connection with commercial shale oil production, there has been an increase in interest to high-carbon formations sediments. On the Russia territory, one of these objects is the Domanik black shale (also call Domanikites) deposits of the Russian platform [1, 2, 3]. From one side such deposits are considered as oil-saturated rocks; from another side are unconventional reservoirs [4, 5, 6, 7]. The main part of the Domanikites is confined to carbonate-siliceous carbonaceous complexes of the Domanik horizon of the Francian stage of the Upper Devonian system. Although their manifestations can be traced even higher in the section, up to the Tournaisian stage of the Lower Carboniferous system. According to previous studies in the Domanik formation sedimentary complexes of the Volga-Ural oil and gas province, two types of rocks are distinguished - the Domanikites themselves and Domanikoids. Domanikites contain from 5 to 20% organic matter.

This is indicated in a number of papers [8, 9]. Hydrothermal activity in addition to silica served as a source of biophilic elements, which caused a surge in biota vital activity [10]. Mineralized water of the hydrothermal solutions rose upwards and carried various chemical elements, including elements...
important for the life of the plankton. This stimulated rapid life activity in the seas and accompanied (after the death of organisms) by the accumulation of large quantities of organic matter in the sediments. At the same time, there was a periodic change in the oxidation-reduction potential. Periodic reducing conditions contributed to the preservation of organic matter. Therefore, the organic matter is preserved in the carbonate-siliceous layers [11, 12, 13].

As a rule, they occupy territory of uncompensated depressions in the Famennian stage rock formation basin. Domankoids contain less than 5% organic matter. They are developed both in axial and onboard zones of the Kama-Kinelsky system of depression (KKSD) in the Mendym horizon deposits. Both types of carbonaceous rocks have a practically similar lithological composition. The difference between them lies in variations in siliceous component content and number of authigenic minerals. If content of very fine-grained silica was determined by primary sedimentation factors, then authigenic minerals are indicators of secondary lithogenesis processes. In this work, an attempt is made to compare organic matter content with dolomite mineralization, which is an active agent in mineral formation.

1.1. Object

The object of study was core material of several deposits, selected from the Semiluk and Mendym horizons of the Upper Devonian formations from the Volga-Ural region, Russian Federation (figure 1). Tectonically the studied wells are confined to the eastern side of the South Tatar and North Tatar Arches and to the western slope of the Melekess Depression. A feature of the studied object is high facies variability of sediments; a high content of organic substances, including hydrocarbons; high porosity and very low permeability. These rocks are distributed along the eastern part of the Russian platform. Depth of occurrence of such deposits varies from 1630 to 1900 m. The thickness of the sediments usually does not exceed 20-30 m. Current temperatures of rocks do not exceed 30°C.

![Figure 1](image-url)  
**Figure 1.** Volga-Ural oil-bearing basin: a – Location in European part of Russia; b – Tatarstan republic and location of studied fields; c - Stratigraphy and general lithology of Fransian stage in the Tatarstan.

In sections of all the studied wells, an alternation of three main lithological rocks is observed: 1) carbonate-siliceous rocks enriched with organic matter, 2) limestones (mudstone, wackstone) and 3) clastic (lithoclast or rudstone) limestones composed of carbonate fragments cemented by carbonate-siliceous material, enriched with organic matter.

Carbonate-siliceous rocks enriched with organic matter are dense, cryptomeroous domanikites and domanikoids of dark gray and black color. Color variations are determined by organic matter content.
In sections, rocks form layers up to the first tens of centimeters thick. Often alternate with carbonate rocks.

Limestones macroscopically have cryptomerous structure. Under the microscope rock structure is usually pelitomorphic (mudstone). Less often, a small amount of organic residues, bioclasts (wackstones), is found in limestones. Usually found in the form of small in thickness (from a few millimeters to the first tens of centimeters) layers alternating with carbonate-siliceous rocks. The rocks are light gray, dense, usually with massive texture. Virtually do not contain of organic matter.

Carbonate breccia (lithoclast limestones). A diagnostic sign is their fragmental structure. They can be found in various areas of sections. The power of such formations is up to tens of centimeters. They are rocks composed of weakly rounded fragments of light gray limestone, cemented with dark gray carbonate-silicon-carbonaceous material.

2. Methodology

Considering the cryptomerous structure of rocks, the main research methods were optical-microscopic, X-ray and thermal analysis methods. Optical microscopic analysis was carried out on a CarlZeiss Axio Imager A2 polarizing microscope equipped with high-resolution camera. X-ray analysis was carried out on a Bruker D2 Phaser diffractometer. Thermal analysis of the rocks was carried out on a NETZSCHE STA 449 F3 Jupiter instrument, which made it possible to record both loss mass of rock and manifestation of exo- and endo effects in thermal transformations process of organo-mineral components. The main research methods also include SEM analysis performed on an XL-30ESEM electron microscope (FEI, Philips, Netherlands) equipped with an EDAX energy dispersive spectrometer (USA). As additional methods, X-ray fluorescence analysis, analysis of fluid inclusions in dolomite and homogenization temperatures, petrophysical properties of rocks, study of organic matter by Rock-Eval and geochemical methods were used.

3. Results and Discussion

3.1. Optical microscopy data

According to optical microscopy, authigenic dolomites are found both in the form of isolated, non-touching crystals, and in the form of dense aggregate clusters. In intergrowths, rhombohedral crystals of dolomites come into contact mainly with faces. Dark brown clumps of condensed organic matter are observed between the grains. At some sites very fine-grained dolomite completely replaced calcite cement of the rock and performing the function of cementing material. Most authigenic dolomite is associated with black puffs and lenses enriched by organic matter. Figure 2a shows a fragment of a stylolite seam, the cavity of which is intensively pigmented with organic matter. Secondary dolomitization in form of rhombohedral crystals forming fine-grained aggregates is observed in the stylolite seam cavity.

The dolomite grains size in the studied sediments varies widely from 0.01 to 0.4 mm. Grains usually have an isometric, less often irregular shape. Among them, pronounced rhombohedra stand out, forming isolated individuals or small clusters. Cleavage cracks, relics of primary pelitomorphic calcite, clay-bituminous matter are noted in the largest dolomite grains. In association with dolomites, pyrite frambooids up to 0.15 mm in size and small grains of authigenic calcite are noted. Quartz, feldspar, and rare muscovite flakes act as accessory minerals.
Figure 2. Photo of limestone with stylolite seam (a) and dolomite crystals (b) at different increase. Both in polarized light.

3.2. Electron microscopic data

Electron microscopic studies confirmed the relationship between authigenic dolomites with areas enriched by organic matter (figure 3a). Dolomite is found in the form of hipidomorphic crystals of rhombohedral habitus ranging in size from 0.05 to 0.15 mm. The crystals contacts with the host rock are sharp, even, often underlined by kerogen rim. In domanikites, dolomitic newly formed structure are at different stages of formation. Together there are perfect crystals with well-developed edges and faces, and partially crystallinity types. In individual samples of domanikites, dolomite crystals form irrational intergrowths. Relatively perfect (even) faces of dolomite crystals are complicated by growth microdefects in the form of unfilled holes. Apparently, holes on the authigenic dolomites faces formed due to local blocking of crystal growth by kerogen films. The spaces between crystals are filled with organic matter. According to microprobe analysis dolomites are nonstoichiometric. In crystal lattice of the mineral, calcium ions prevail over magnesium ions. The constant presence of iron lines in the spectra indicates that lack of magnesium ions in dolomite is partially compensated by Fe2+ ions. Dolomite grains which metasomatic replacing limestones are more stoichiometric and do not contain iron ions in the crystal structure.

3.3. Thermal research methods data

Some of the domanikites samples folded by dolomites in association with coarse-grained calcite were investigated by the thermobaric geochemistry method to determine homogenization temperature of gas-liquid inclusions. The data obtained show that the average temperature of inclusions homogenization which found in secondary calcites is 117°C, the minimum is 97°C, and the maximum is 137°C. Given location proximity of syngenetic dolomites with them, it can be assumed that the dolomitization process occurred at similar temperatures.

The organic component of the samples was identified by thermal analysis of exothermic effects in temperature range up to 600°C (DSC curve), and its quantitative content was estimated by the TG curve. The first exothermic effect and associated mass loss in temperature range 110-375°C (figure 3b) corresponds to thermal decomposition of light hydrocarbon fraction. A similar effect in range of 375-490°C corresponds to the destruction of the heavy hydrocarbons fraction.

Thermal decomposition data of organic matter, it was found that the maximum amount of C_{org} is associated with carbonate-siliceous rocks (5-15%). Moreover, the more silica in them - the more C_{org}. 
According to the content of $C_{\text{org}}$, these rocks correspond to the definition of domanikites. In carbonate rocks, the $C_{\text{org}}$ content does not exceed 5%, i.e. these are typical domanikoids. The lowest content of $C_{\text{org}}$ is noted in carbonate breccias (less than 1%). Here, organic matter is concentrated in carbonate-clay cement of rocks, which binding lime fragments. An analysis of organic matter fractions ratio in the Domanik horizon rocks of showed that, despite their lithotype, heavy hydrocarbons prevail in association with medium hydrocarbons. Light fractions hydrocarbons are either absent or in small quantities. Moreover, in all cases, there is a tendency to an increase of light hydrocarbons in dolomitization areas. In some wells, where secondary dolomites form small interlayers, dark brown oil stainings are noted in cavities and pores spaces of dolomite metasomatites. Thus, there is a clear relationship between light hydrocarbons of oil series and dolomitization processes (figure 4 a, b).

Figure 3. SEM photo of secondary dolomite in carbonate-siliceous rocks: a – dolomite crystals in carbonate-siliceous carbonaceous complexes of the Domanik horizon; b - authigenic hipidiomorphic dolomites crystals of rhombohedral habitus.

Figure 4. Data of X-ray (a) and thermal analysis (b): blue – differential scanning calorimetry curve (DSC), black – thermogravimetric curve (TG).

3.4. Secondary dolomitization characteristic

Taking into account structural features of secondary dolomites, the homogenization temperature of gas-liquid inclusions in calcites accompanying them, and paragenesis with light hydrocarbons, dolomitization processes can be considered as indicators of oil-water fluids migration. During fluid
dynamic activation periods of the Volga-Ural anteclise and heating of sedimentary stratum by endogenous heat of the Earth, deep gas-water hydrocarbon-containing fluids experienced upward migration [14]. The emanations of oil deposits from underlying the Middle Devonian oil-saturated sandstones, passed through the Domanik horizon deposits, saturating rocks pore space by light hydrocarbons and their accompanying carbon dioxide. At the same time, in thin pores local areas of domanikites and domanikoids an increased partial pressure of CO$_2$ was created. Under these conditions were activated the processes of calcite dissolution in limestones which associated with carbonate-silicon-carbonaceous layers of domanikites. High-carbon rock sections with increased porosity and high sorption capacity, in comparison with dense carbonate layers, were a kind of reservoirs where Ca$^{2+}$, Mg$^{2+}$ and Fe$^{2+}$ ions accumulated, migrating as part of gas-water hydrocarbon-containing fluids. As the CO$_2$ content in system decreased, dolomite crystals formed from pore solutions. As they grow, due to crystallization pressure, dolomite crystals move apart of surrounding organic matter, acquiring an idiomorphic rhombohedral habit. The lack of Mg$^{2+}$ ions in solutions led to nonstoichiometric dolomites formation in which Ca$^{2+}$ and Fe$^{2+}$ ions occupy a part of magnesium structure in the crystal structure. The presence of kerogen in surrounding crystallization environment, which capable of blocking crystal growth, caused a high content of growth defects on authigenic dolomites faces. Over time, part of light hydrocarbons underwent biochemical oxidation. The result of this process was appearance of pyrite frambois developing on dolomites and an increase in amount of medium and heavy oil fractions [15] in organic matter composition.

It is also worth noting that the observed dolomite crystals formed on fluid migration ways are found on throughout the studied territory. An analysis of the Kama-Kinelsk system of depression (KKSD) profile for region and the wells position does not show any connection between dolomitization process in deposits with axial, edge, side or shelf region of the KKSD. There is also no definite connection with strata lithological composition. The totality of data and observations may indicate a regional scale of upward fluid migration through the carbonate-siliceous strata of domanikites.

4. Conclusions

Summing up the obtained results, we can draw to the following conclusions:

1. Secondary dolomitization of the Domanik horizon high-carbon rocks is local, focal, character. Authigenic dolomites are associated mainly to organic matter enriched areas. Dolomites form either separate grains of rhombohedral habit or dense aggregate intergrowns with organic matter pinched between the grains.

2. Authigenic dolomites are characterized by a nonstoichiometric crystallochemical structure due to presence in magnesium positions ions of calcium and iron. Such structural defects are caused by deficiency of magnesium ions in mineral-forming solutions. The faces of dolomite crystals are complicated by growth defects due to local blocking by kerogen of some areas on growing crystals surface.

3. Large calcite grains, paragenetically associated with dolomites, according to gas-liquid inclusions homogenization temperature, were formed at crystallization environment temperatures from 100 to 130°C. It can be assumed that the calcite-dolomite association was formed during period of fluid-thermal activation of the Volga-Ural anteclise central part.

4. High contents of light hydrocarbons and oil stainings in rocks areas subjected to dolomitization indicate about connection between dolomitization processes and water-oil and gas fluids migration from downstream oil deposits. Given ubiquitous presence of authigenic dolomites within various tectonic structures bounds, it can be concluded that the process of deep upward fluid migration was regional in nature.
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References

[1] Zaydel'son M, Vaynbaum S, Koprova N 1990 19
[2] Bazhenova T 2009 Geology and Geophysics 50(4) 412-424
[3] Zharkov A 2015 Oil and Gas Geology Theory and Practice 10(4) 1-14
[4] Gordadze G, Tikhomirov V 2007 Petrochemistry 47(6) 422-431
[5] Kiryukhina T, Fadeeva N, Stupakova A 2013 Geology of Oil and Gas 2 76-87
[6] Ul'mansky F, Bazarevskaya N 2013 Georesource 52 21-25
[7] Fadeyeva N, Kozlov E, Poludetkina E 2015 Bulletin of Moscow University 6(4) 44-52
[8] Vinokurov S, Gottikh R, Pisotsky B 2010 Geochemistry 4 377-389
[9] Gottikh R, Grunis E, Pisotsky B 2007 Geology of Oil and Gas 2 60-70
[10] Khain V, Polyakova I 2012 Oceanology 52(3) 423-436
[11] Bushnev D 2009 Reports of the Academy of Sciences 426(4) 516-519
[12] Lukin A 2013 Geology and Minerals of the World Ocean 4 5-28
[13] Kayukova G, Feoktistov D, Pronin N 2017 Neft. Khoz. Oil Industry 12 86-89
[14] Korolev E, Plotnikova I, Kamaleeva L 2012 Geochemistry International 50(11) 964-973
[15] Mikhailova A, Kayukova G, Vakhin A 2019 Petroleum Sci. and Techn. 37(4) 374-381