

Research Article

The Oil-Bearing Strata of Permian Deposits of the Ashal'cha Oil Field Depending on the Content, Composition, and Thermal Effects of Organic Matter Oxidation in the Rocks

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The features of the oil-bearing capacity of the productive strata of Permian deposits in the interval of 117.5–188.6 m along the section of individual wells of the Ashal'cha field of heavy superviscous oil (Tatarstan) were revealed depending on the content, composition, and thermal effects of organic matter (OM) oxidation in the rocks. It is shown that the rocks are very heterogeneous in their mineral composition and in the content of both free hydrocarbons by extraction with organic solvents and insoluble OM closely associated with the rock. The total content of OM in rocks varies from 1.72 to 9.12%. The features of group and hydrocarbon composition of extracts from rocks are revealed depending on their mineral composition and the content of organic matter in them. According to the molecular mass distribution of alkanes of normal and isoprenoid structure, extracts from rocks are differentiated according to three chemical types of oil: type A¹, in which n-alkanes of composition C₁₄ and above are present, and types A² and B², in which n-alkanes are destroyed to varying degrees by processes microbial destruction, which indicates a different intensity of biochemical processes in productive strata of Permian sediments. These processes lead to a decrease in the amount of OM in the rocks and an increase in the content of resins and asphaltenes in the oil extracted from them, as well as an increase in the viscosity of the oil. Using the method of differential scanning calorimetry of high pressure, it was found that the studied rock samples differ from each other in quantitative characteristics of exothermic effects in both low-temperature (LTO) 200–350°C and high-temperature (HTO) 350–600°C zones of OM oxidation. The total thermal effect of destruction processes of OM depends on the content of OM in the rocks and its composition. The research results show that when heavy oil is extracted using thermal technologies, the Permian productive strata with both low and high OM contents will be involved in the development, and the general thermal effect of the oxidation of which will contribute to increased oil recovery.

1. Introduction

The huge amount of heavy oil and natural bitumen resources are concentrated in the territory of Tatarstan, in deposits of Permian system [1–10]. The development of heavy oil fields seems to be an important and urgent task in respect of strengthening the hydrocarbon resource base and maintaining oil production at the proper level. Most of the

explored deposits of heavy oil and natural bitumen in Tatarstan are concentrated in the Kazan and Ufa deposits of the Permian system and are associated with the main part and the western slope of the South Tatar Arch (STA) and the eastern side of the Melekes Depression [4–6, 9, 11]. Currently, in pilot development are deposits of heavy oils from the Mordovo-Karmalsky and Ashal'cha oil fields are associated with bundle of sand of the Sheshmin

horizon of the Ufa deposits [3, 4, 10–14]. In the complex under development, more than 58 fields of heavy oils and natural bitumens have been found; most of which have been studied with varying degrees of detail.

An analysis of the occurrence conditions of the deposits of the sandy bundle of the Sheshmin horizon shows their complex and heterogeneous structure within the Permian deposits of the structural zone of the western STA slope [9, 15]. In the article [15], the main focus is on identifying of influence of sedimentation conditions on the structure and reservoir properties of sediments containing bitumen (oil), as well as on the properties of the fluids contained in them. The revealed features of changes in the reservoir properties of rocks and bitumen saturation along the section of a sandy bundle of the Sheshmin horizon can be the result not only of changing conditions for the formation of sediments but also the result of the influence of post sedimentation processes, as a result of calcification or redistribution of carbonate cement in the rock under the influence of aggressive fracture products (oxidation, biodegradation) oil deposits. The sandstones of the Sheshmin horizon form traps that can be combined into specific zones with certain conditions of their formation, development history and structural features, which determined the conditions of occurrence, the placement, and the distribution ratio of formation fluids—heavy oils, bitumens, and formation waters. Studies of many authors [1, 2] showed that the conditions of occurrence of heavy high-viscosity oil and natural bitumen deposits in Tatarstan largely determine their composition and nature of saturation of the rock with bitumen, and ultimately depend on the choice of areas of exploration and methods for their development.

The most widely used methods for the extraction of heavy oils and natural bitumens are steam-thermal treatment of well bottom-hole zones and injection influence of heat into the formation [12–19]. Increased oil recovery under the influence of heat is achieved by reducing the viscosity of the oil, which helps to improve its coverage, increasing the displacement coefficient. However, many issues still remain unresolved. Works on finding optimal technologies aimed at increasing the efficiency of developing deposits of heavy oils and natural bitumens using thermal methods are carried out in many research centers and oil-producing companies [15–27]. Difficulties arising from the development of heavy oil fields are associated with two problems: first, unfavorable reservoir properties—low thermal conductivity, low permeability, and lack of reservoir energy; second, the hydrocarbon component of the bituminous reservoirs is in an inactive state [4, 7, 10, 12, 13, 15, 19]. The immobility of hydrocarbons in the Permian strata is associated with its quality and with the geological and environment conditions. Therefore, for successful development of heavy oil fields requires information about the properties of oil-bearing rocks, which ensure the formation of oil deposits and determine their preservation or destruction over time, the properties and quality of the fluids contained in them, and also the features of the chemical reactions of oxidation of hydrocarbons in reservoirs when using thermal technologies during development.

The objective of the work is to conduct comparative studies of the material composition of rocks from the productive

strata of the Permian deposits of the Ashal'cha oil field for evaluation their oil-bearing capacity depending on the content and quality of organic matter in the rocks and also the amount of heat generated during its thermal oxidation in the rocks.

2. Materials and Methods

2.1. The Object of Study. The object of the research was a collection of rock samples taken from a depth interval from 117.5 to 188.6 m from different wells of productive strata of the Permian deposits of the Ashal'cha heavy superviscous oil field, located on the western slope of the STA (Figure 1), which is developed using modified Steam-Assisted Gravity Drainage technology (SAGD) [12–15].

Ashal'cha oil field was discovered in the year 1960. Geologically, the field belongs to the Volga-Ural petroleum province and is an unconventional oil reservoir, with seven productive horizons in the section, which in turn are subdivided into strata and seams. Productive deposits are terrigenous Devonian reservoirs ($H = 1698$ m), Lower Carboniferous ($H = 1061.7$ – 1064.4 m), Devonian carbonate rocks ($H = 1068.6$ m), and Middle Carboniferous ($H = 769.1$ – 795.6 m). In this oil field, 23 oil deposits have been identified, which practically coincide in terms of productive horizons. Oils of Devonian deposits are a type of sulfur, paraffin, resinous. The composition of oil from coal deposits is with high sulfur, paraffin, and high resin content. At this field, in the Permian sediments at a depth of 0–400 m from the surface, significant reserves of heavy super-viscous oils and natural bitumen were revealed. The object of industrial development of the heavy oils is the Sheshmin horizon of the Ufa deposits. Production is carried out by PJSC TAT-NEFT using both vertical and horizontal wells. The initial temperature in the reservoir of this field is about 8°C, pressure 0.44 MPa [11]. The oil produced is characterized by high dynamic viscosity (up to 4100 mP s at 20°C) and high density (up to 966 kg/m³ at 20°C), with high sulfur content (4.8–5%), resins, and asphaltenes. Mass fraction of paraffin is 1.0–1.6%. The pour point of oil varies from -5 to -12°C. Steam injection to the reservoir at temperature of 150–290°C provides heating of the strata and these conditions, the viscosity of the oil decreases [28], but its composition does not change significantly. In the course of further storage, the viscosity increases again and the oil becomes slow-moving, which creates certain problems for its further transportation to the refinery [16].

2.2. Experiments and Methods. The mineral composition of rock samples from the Ashal'cha oil field was investigated by X-ray diffraction method. The diffraction spectra of the gross samples were recorded on a Shimadzy XRD-7000S automatic powder diffractometer, on CuK α radiation with a long wavelength $\alpha = 1.54060$ nm, using a nickel monochromator on a diffracting beam, in increments of one point at a point 3 s; and D2 PHaser Bruker on CuK α radiation with a long wavelength $\alpha = 1.54060$ nm. The processing of the diffraction spectra and the diagnostics of the crystalline phases present are carried out using the original interactive computer system EVA, version 4.0, intended for the study of

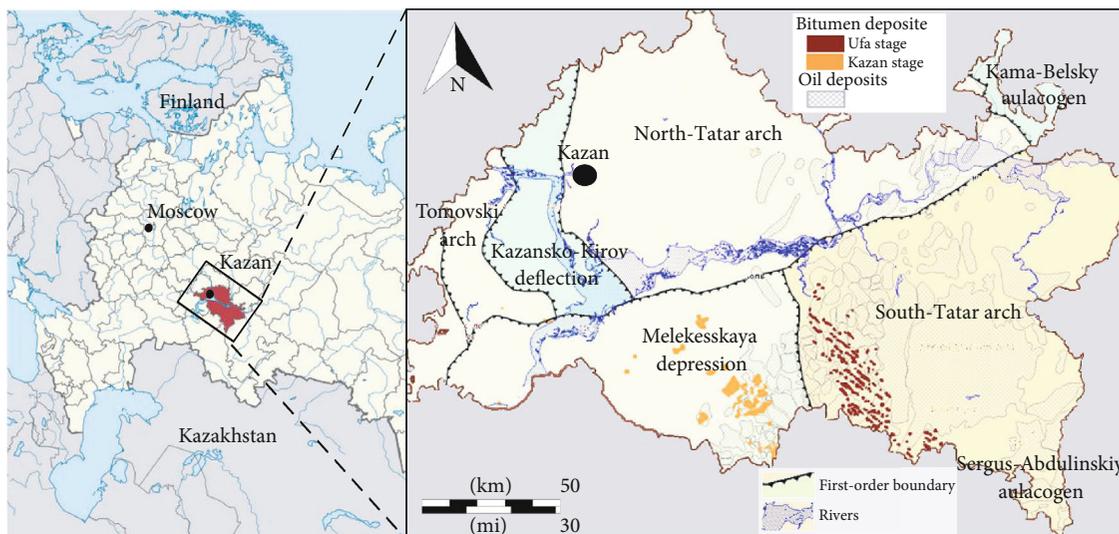


FIGURE 1: Location scheme of heavy oil and natural bitumens reservoirs in the sediments of the Ufa and Kazan stages of the Permian system in Tatarstan (according to the data of the Tatar geological-prospecting control center).

sedimentary rocks and soils, and having specialized ICDD-2010 databases.

Analysis of rock samples for organic matter (OM) content and their thermal stability was performed on a synchronous thermal thermogravimetry and differential scanning calorimetry (TG/DSC), analysis instrument STA 443 F3 Jupiter (Netzsch, Germany) with Netzsch Proteus Thermal Analysis software running under the Windows XP operating system. Measurement conditions are oxidizing environment (air), heating rate 10°C/min, and temperature range 20–1000°C. The TG-DTA curves were processed on a computer using Netzsch Proteus Thermal Analysis standard software.

Using the differential high-pressure scanning calorimeter Netzsch DSC HP 204 Phoenix Thermal Analyzer STA 449 F1 Jupiter (Netzsch, Germany), the maximum phase transition temperatures were determined and the values of thermal effects manifested as a result of oxidation reactions of various OM agents from the Permian deposits of the Ashal'cha oil field were calculated. Experimental conditions are atmosphere—air, temperature range of the study from 30 to 600°C, heating rate 10°C/min, supported pressure of the experiment 5 MPa, dynamic flow rate 10 ml/min, and crucible material—aluminum (with a punctured lid). The sample weight is 1.73–1.74 mg. Before the experiment, samples of rocks were exposed for 10 min at 30°C. The device is calibrated by temperature on standard samples (metals of high purity) on four melting points: In, Sn, Bi, Zn. Calibration of the sensor (heat flux value) was also carried out at four given points. To eliminate the influence of the operation of the device, calibration by thermal resistance was also used at four points.

To isolate hydrocarbons from rock, samples were extracted in the Soxhlet apparatus with a mixture of solvents: chloroform, benzene, and alcohol benzene, taken in equal proportions. The sample of rocks was crushed to a particle

size of 0.25–0.50 mm. The extract yield was calculated on the mass of the initial sample of the rock [29].

Using the SARA method of analysis [30], extracts from rocks were divided into four fractions: asphaltenes, saturated hydrocarbons, naphthenic-aromatic compounds, and polar aromatic compounds—resins. Asphaltenes were pre-precipitated from the initial products in 40-fold amount of hexane. The maltenes were separated by liquid adsorption chromatography on alumina calcined at 425°C on saturated hydrocarbons by elution with hexane adsorbent, aromatics, eluting with toluene, and the resins were displaced from the adsorbent with a mixture of solvents: benzene and isopropyl alcohol, taken in a ratio of 1:1.

The study of the hydrocarbon composition of extracts from rocks was carried out on the Kristal 2000M instrument using capillary gas chromatography (GC) in temperature programming mode from 100 to 300°C: in the temperature range from 100 to 150°C, the temperature in the thermostat changed at a rate of 10°C per minute, in the range from 150 to 300°C—3°C/min, respectively. Hydrogen was used as carrier gas. The temperature of the evaporator is 310°C, and the temperature of the detector is 250°C.

3. Results and Discussion

3.1. Characteristics of Rocks by Thermal and X-Ray Diffraction Methods. The method thermogravimetric of thermal analysis and differential scanning calorimetry (TG/DSC) is widely used to determine the potential content of OM in bituminous rocks and its thermal stability [31–34]. According to data of the thermal analysis (TG) for the rock samples, mass loss in different temperature ranges from 20 to 1000°C is distinguished (Table 1). The OM content in rock samples was estimated on base of its mass loss in the temperature range 200–600°C [27]. Significant mass loss at temperatures above 600°C may be associated with dissociation of carbonate

TABLE 1: The data of thermal analysis of rock samples from the Permian sediment of the Ashal'cha oil field.

Sample no.	Depth (m)	Mass loss of the rock samples (wt%) in temperature ranges from 20 to 1000°C					Σ OM	F^{**}
		20-200	200-400	400-600	600-800	800-1000		
Well 24								
1	117.5-118.5	2.13	5.09	4.03	2.34	0.36	9.12	1.26
1*		0.52	0.74	1.38	2.97	0.06	2.12	0.54
2	121.5-123.5	1.25	3.52	3.26	3.60	0.22	6.78	1.08
2*		0.41	0.73	1.26	5.21	0.01	1.99	0.58
3	129.0-132.0	0.71	1.25	1.76	12.81	0.28	3.01	0.71
3*		0.40	0.56	1.16	11.86	0.01	1.72	0.48
Well 9								
4	141.6-148.6	0.40	1.68	1.31	5.29	5.25	2.99	1.28
5	148.1-149.7	0.36	1.49	1.60	5.36	1.83	3.09	0.93
6	152.9-154.9	0.39	1.19	1.20	4.65	0.54	2.39	0.99
Well 106								
7	174.4-177.6	1.26	2.61	2.61	1.88	0.18	5.22	1.00
8	187.0-188.6	1.79	4.52	4.00	1.85	0.14	8.52	1.13
Well 107								
9	176.5-178.0	1.93	4.51	3.85	2.09	0.14	8.36	1.17
10	181.0-182.7	0.92	2.91	2.56	3.50	0.19	5.47	1.14
11	185.0-187.0	0.90	2.18	2.13	6.48	0.04	4.31	1.02

*Rock samples after extraction of organic matter; ** $F = \Delta m_1(200-400^\circ\text{C})/\Delta m_2(400-600^\circ\text{C})$.

rocks. Mass loss at temperatures from 20 to 200°C is due to evaporation of light hydrocarbons and adsorbed water by clay minerals.

The OM content in the studied samples of rocks from different wells varies from 2.39 to 9.12% that indicates on the heterogeneity of their oil-generating potential. A decrease in the OM content is observed from the upper part of the section to its lower part in the depth intervals of 117.7-132 m (well 24) and 176.5-187 m (well 107). The composition of OM is also changing, which is reflected in the values of fractional index $F = \Delta m_1(200-400^\circ\text{C})/\Delta m_2(400-600^\circ\text{C})$, which is the ratio of light and medium OM fractions to its heavy part [33].

After extraction of free hydrocarbons from the rock, a certain amount of OM remains in it, which is not extracted by organic solvents. This is mainly the heavy part of organic matter, which is subject to destruction mainly in the temperature range of 400-600°C. It is clearly seen from the diagrams showing the mass loss of rock samples before and after extraction, for example, rock samples from well 24 (Figure 2). Attention is drawn to the large mass loss of rock samples from the depth interval 129-132 m of the lower part of the section well 24 at temperatures above 600°C (Figure 2) that is apparently due to the dissociation of carbonate rocks during temperature exposure. In this sample of rock according to X-ray analysis, 26.84% falls on calcite.

The rock samples were investigated by X-ray diffraction method in order to evaluate the influence of clay or carbonate mineral compositions of reservoir rocks on the compositional changes of hydrocarbon fluids (Figure 3). In rock samples from well 24 (117.5-132 m), from 27 to 38% is accounted

for quartz and from 19.4 to 39.6% to albite, one of the most common rock-forming minerals, which is white sodium feldspar of magmatic origin, a class of silicates, aluminosilicate of the plagioclase group. In the upper depth interval of 117.5-118.5 m, the content of calcite is 4 times less than in the lower part of the section (6.96 against 26.84%), while the content of quartz is rather high and amounts to 39.7%. In this interval of depths, the most oil-saturated rock is obtained, which follows from the data on the content of OM in it (Figure 4).

High calcite content in rock samples from the interval of 141.6-154.9 m (well 9). Thus, in the rock sample 5 from the depth interval 148.1-149.7 m, the calcite content is 41%, quartz accounts 26%, and 23% accounts for albite. In all rock samples from this well, clinoclone is present in the amount of 3-4%, mineral, sheet aluminosilicate of iron and magnesium, the most common member of the group of chlorites. There is a correlation with the correlation coefficient $r = 0.72$ between the OM content in rocks and the calcite content in them (Figure 4), namely, with an increase in the content of calcite in the rocks of the lower intervals of the productive strata, the OM content decreases compared to the upper oil-saturated rocks by enriched clay minerals.

In the article [22] using the Rock-Eval pyrolysis method, oil-generating potential of bituminous rock samples from the Permian deposits of the Ashal'cha oil field was estimated. It is shown that Permian rocks contain a high content of free hydrocarbons, after extraction, which the oil-producing potential of rocks sharply decreases. The residual organic matter is characterized by low values of the hydrogen index, high values of the oxygen index, and a low degree of maturity,

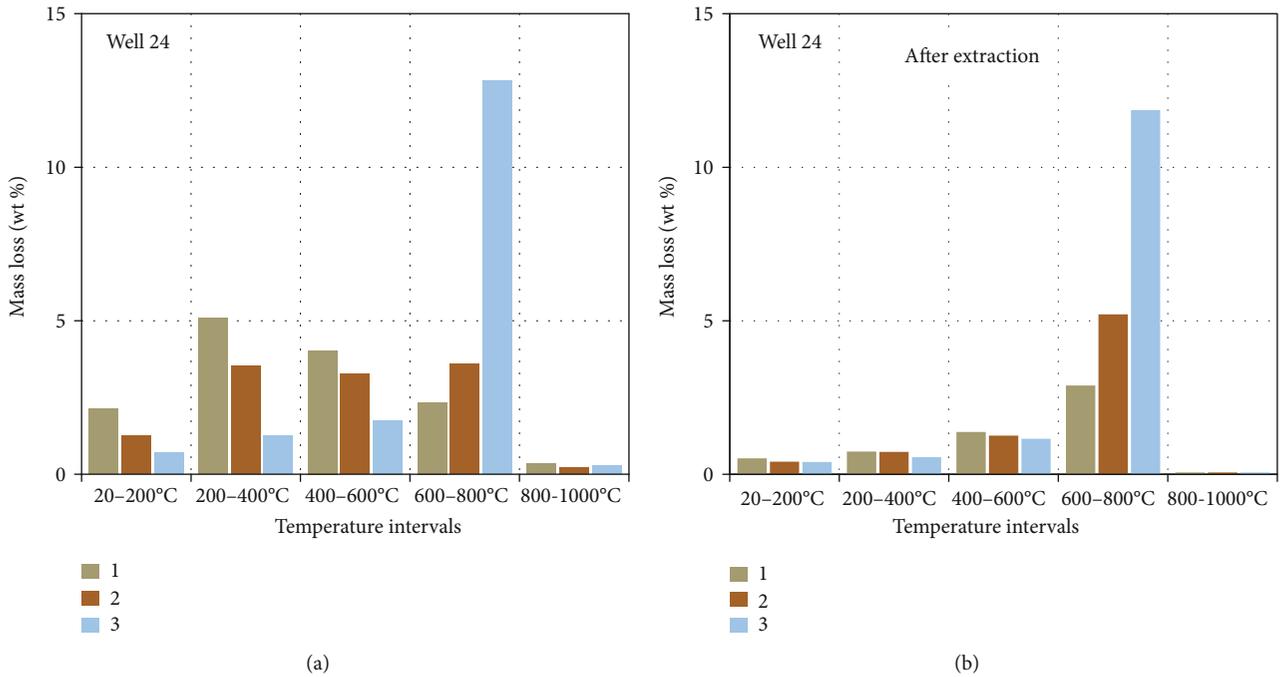


FIGURE 2: Diagrams of the mass loss of bituminous rocks by well section 24 according to thermal analysis. (a) Initial rock. (b) Rock after extraction. Intervals of sampling depths: 1—117.5–118.5 m; 2—121.5–123.5 m; 3—129–132 m.

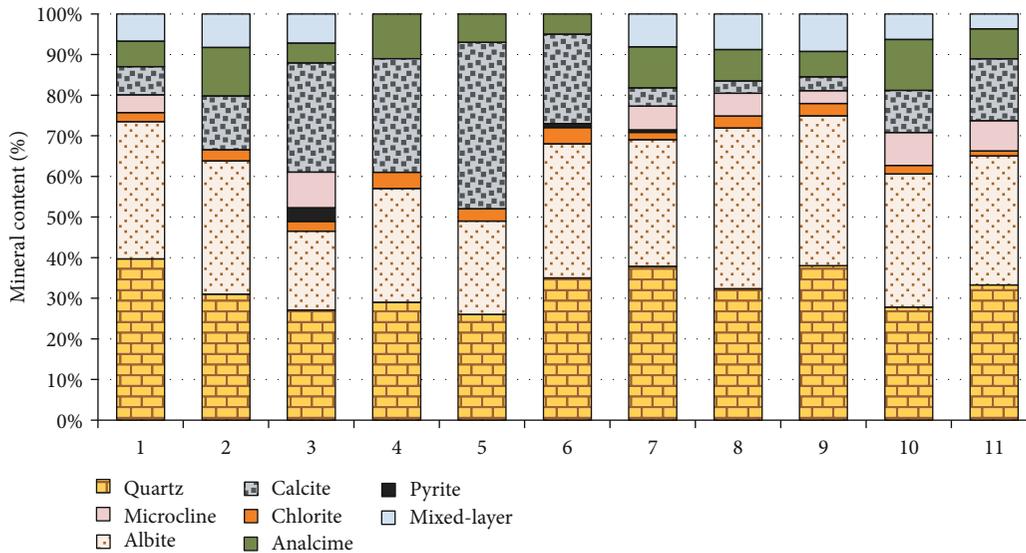


FIGURE 3: Diagram of the mineral composition of samples of rocks from the Permian deposits of the Ashal'cha oil field from the following intervals: well 24—117.5–118.5 m (1), 121.5–123.5 m (2), 129–132 m (3); well 9—141.6–148.6 m (4), 148.1–149.7 m (5), 152.9–154.9 (6); well 106—174.4–177.6 m (7), 187–188.6 (8); well 107—176.5–178 m (9), 181–182.7 m (10), 185–187 m (11).

which is typical for kerogen of type III, formed from the sediments of the continental type. It suggests that the pyrolysis parameters are mainly affected not by kerogen degradation products, but by resin-asphaltene components, apparently transformed of migratory oils in Permian deposits. The migratory nature of hydrocarbons is also confirmed by low T_{max} values.

The observed changes in the mineral composition of the rocks studied also affect the reservoir properties of the rocks

and, therefore, determine the oil saturation by the section of the sandstone pack of individual wells. But these changes can be the result of not only changing conditions for the formation of sediments but also the result of influence, post sedimentation processes. As noted above [5, 9, 15], calcitization and redistribution of carbonate cement in the rock may be the result of exposure to aggressive products of destruction (oxidation, biodegradation) of oil deposits occurring in the surface strata of the Permian system. This is consistent with

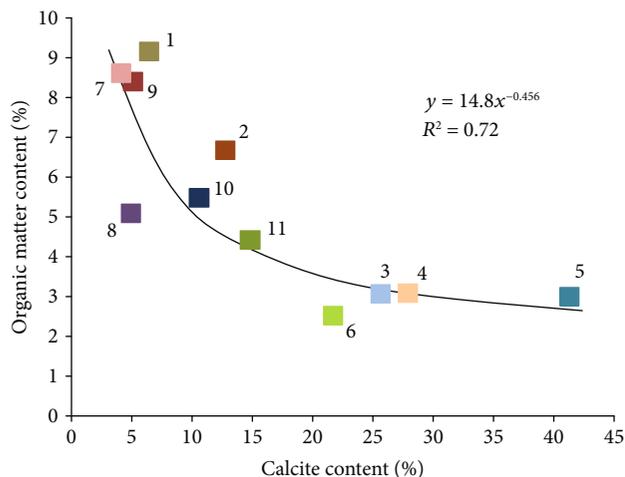


FIGURE 4: Relationship between the organic matter (OM) content and calcite content in rocks: 1—well 24 (samples 1, 2, 3); 2—well 9 (samples 4, 5, 6); 3—well 106 (samples 7, 8); 4—well 107 (sample 9, 10, 11).

the previously identified regularities [9, 10] that the lower parts of the sections of Permian bitumen deposits are usually composed of cemented weakly porous (5-12%) sandstones. In the upper interval, bituminous saturation is usually higher than about 50 vol.% of pores. The lower interval is characterized by a sharp decline in bitumen saturation—up to 20-30% and below.

3.2. Group and Hydrocarbon Composition of Extracts from Rocks. A comparative study of the group composition of extracts from the rocks in the section of individual wells of the Ashal'cha oil field confirms the view that oxidative processes occur in certain zones of the reservoir leading to the destruction of hydrocarbon deposits. (Table 2). In samples of rocks down the section from the studied wells, the content of free hydrocarbons decreases, as evidenced by a lower yield of extracts from them and noticeable changes in their group composition. So, in extracts from rock samples from deeper sampling intervals of 129-132 m and 185-187 m wells 24 and 107, respectively, the content of asphaltenes increases.

For extracts from rocks selected from the depth interval 174.4-177.7 m of well 106, a reverse pattern is observed: as the depth of the strata increases, the content of saturated hydrocarbons increases and the asphaltenes content more than halves. A similar pattern is observed in the composition of extracts from the depth interval of 141.6-154.9 m (well 9). It is possible to note a relatively low yield of extracts from the rocks of this well and a rather high content of asphaltenes and saturated hydrocarbons in their composition. Changes in the content of aromatic compounds and resins in the studied rock samples are not sharp. The resin content is close enough for all rock samples from wells 24 and 107, despite noticeable differences in their sampling intervals. Deposition of asphaltenes and paraffin in productive strata of wells is a serious problem [35, 36]. Negative

phenomena in porous formation media, in the wellbore and production pipelines, coking difficulties in oil refining processes, as a rule, arise from the occurrence of this phenomenon.

According to the established facts [3, 5, 9, 10], the most contrasting differentiation of natural bitumens and superviscous heavy oils by their physicochemical properties in the Permian sediments in Tatarstan is associated with different geochemical conditions of their occurrence relative to water levels in river valleys—erosion bases. The fact is that the hydrogeological regime of deposits and the intensity of chemical and biochemical processes affecting hydrocarbons largely depend on these conditions, leading to their destruction. The deposits of bitumen are controlled by vault type traps, which are formed either by elevations of the third and second orders of the modern structural plan of the Permian sediments or by positive structural forms of sedimentary nature. There are also observed interfaces between the bitumen deposit and the aquiferous part of the reservoir, similar to the oil-water contacts, which also lead to the erosion of bituminous formations and the oxidation of bitumen. Therefore, even in the same stratigraphic horizon, deposits of heavy oils and bitumens find themselves in different geochemical conditions and are subjected to varying degrees to the influence of hypergene factors.

Separation by the SARA method in conjunction with other methods to characterize the crude oil, due to its complexity, allows not only to identify changes occurring in individual structures of oil but also allows you to predict the effect of various processes on oil. According to Petrov's chemical classification by gas chromatography method (GC) [37], extracts from rocks can be attributed mainly to oils of three chemical types: A^1 , A^2 , and B^2 , differing in the molecular mass distribution of alkanes of normal and isoprenoid structure, which indicates different stages of their biochemical degradation (Figures 5–8). This suggests that the differences in the hydrocarbon composition of extracts from the Permian deposits of the Ashal'cha oil field are determined by the influence of local factors. Based on chromatograms in the depth interval 117.5-132.0 m along the section of well 24, regardless of the mineral composition of the rocks, there is type B^2 oil in which n-alkanes are absent or are contained in small quantities; for the most part, isoprenoid alkanes are predominant. Chromatograms (Figure 5) contain peaks of pristane (C_{19}) and phytane (C_{20}), as well as high-molecular polycyclic biomarker hydrocarbons—adiantan (C_{29}) and hopan (C_{30}) [37]; the ratio of which is constant in all studied extracts from rocks, confirming of their common genetic type. The values of the geochemical indicators of the investigated objects are given in Table 3. There are no significant changes in the molecular composition of oil in the section of the reservoir, although changes in the group composition are very noticeable. The type of oil B^2 is also characteristic of extracts from rock samples taken from a deeper depth interval of 141.6-154.9 m of well 9 (Figure 6), in the mineral composition of rocks of which a high content of calcite is noted. The extracted heavy oil in this field with the use of SAGD also belongs to type B^2 [10]. For B^2 oils of the type of indicator value, $K_i = (Pr + Ph)/(nC_{17} + nC_{18}) > 1$.

TABLE 2: Group composition of extracts from rock samples of the Permian deposits of Ashal'cha oil field (SARA analysis).

Sample no.	Depth (m)	Amount (wt%)	Group composition* (wt%)				SP**
			S	A	R	As.	
Well 24							
1	117.5-118.5	7.43	35.33	36.20	21.72	6.75	0.73
2	121.5-123.5	5.52	30.35	34.84	20.54	14.27	0.81
3	129.0-132.0	0.95	33.42	31.96	19.58	15.04	0.94
Well 9							
4	141.6-148.6	2.27	39.79	25.56	14.20	20.45	1.51
5	148.1-149.7	2.63	39.97	31.34	14.17	14.52	1.20
6	152.9-154.0	1.66	41.68	33.74	12.53	12.05	1.49
Well 106							
7	174.4-177.6	4.71	35.80	33.48	24.58	6.14	0.72
8	187.7-188.6	3.30	44.74	32.73	19.72	2.81	0.91
Well 107							
9	176.5-178.0	6.96	37.86	39.95	15.98	6.21	0.79
10	181.0-182.7	3.35	37.48	36.73	17.49	8.30	0.84
11	185.0-187.0	3.38	39.21	32.03	19.61	9.15	0.94

*S: saturated hydrocarbons; A: aromatic hydrocarbons; R: resins; As.: asphaltenes. **SP = (saturated hydrocarbons + asphaltenes)/(aromatic hydrocarbons + resins) [35].

Extracts from rocks selected from other depth intervals of wells 106 and 107 have their own distinctive features. So, paraffin type A¹ includes extracts from rock samples of deeper sampling intervals of 174.4-188 m (well 106). Their composition contains a homologous series of n-alkanes of the composition C₁₄-C₃₇, among which the high-molecular homologs of the composition C₂₀ and above prevail (Figure 7). The predominance of nC₁₇ and nC₁₈ above pristane and phytane gives grounds to speak of the presence of paraffin-type residual components in the rocks (indicator Ki < 1). This type of oil is typical for lower-lying deposits of the Carboniferous and Devonian age [5, 10]. The extracts from the rock data are essentially asphalt-resin-paraffin deposits. They contain a relatively low content of asphaltenes and a high content of saturated fractions enriched with solid n-alkanes according to GC analysis. This gives reason to believe either the loss of light fractions by paraffinic oil in the process of its destruction or the loss of high-molecular components of paraffinic oil in the process of its migration through porous rocks.

The extracts from the rocks of well 107 are practically from the same depth interval of 176.5-182.7 m as the samples from the well 106, n-alkanes are still present in significant concentrations, but in deeper sediments in the depth interval of 185-187 m, their concentration decreases markedly. On the chromatogram of the extract from this depth interval (Figure 8(c)), only small peaks appear on a high naphthenic background, among which alkanes of isoprenoid structure are identified. The relatively high peaks observed in the elution region of relatively low-boiling hydrocarbons are attributed to *i*C₁₅ and *i*C₁₆ isoprenoids. Alkanes of normal structure are present only in small concentrations, which complicate their identification. The mineral composition of the rock sample from this depth interval contains minerals:

pyrite, calcite, etc., which indicate the possibility of secondary processes that lead to the destruction of the oil reservoir.

For genetic judgments, the geochemical indicators (Table 3), which are pristane/phytane (Pr/Ph), Pr/n-C₁₇, and Ph/n-C₁₈ ratios, as well as "odd/ness," allow to evaluate the redox situation in the early stages of diagenesis and catagenetic and migration processes at subsequent stages of formation of deposits [30, 37-39]. According to the Pr/Ph parameters, all samples fall into the area of restorative marine facial environments of OM sedimentation.

According to the indicators, Pr/n-C₁₇, Ph/n-C₁₈, and Pr + Ph/nC₁₇ + nC₁₈, which may reflect the level of catagenetic OM transformation or the influence of migration and biochemical processes of microbial degradation, the studied samples differ significantly, due to the different contents of n-alkanes [30, 37-40]. It is important to note that the values of these indicators for extracts from rocks well 106 are close to the values typical for oils from rocks below the deposited deposits of the Devonian age in a given area [10]. According to the Pr/n-C₁₇ and Ph/n-C₁₈ parameters, these samples fall into the area of reducing shallow-water marine facial sedimentary environments and the level of catagenetic transformation is mature. For studied rock samples from wells 24 and 107, the values of these indicators primarily reflect the degree influence on the composition of hydrocarbons in rocks, biochemical processes of microbial degradation, which take place in the already formed deposits of heavy oils and natural bitumens in the Permian sediments of sedimentary strata.

According to modern concepts [5, 10], the processes of migration, the formation, and destruction of oil accumulations and natural bitumen in the Permian sediments in Tatarstan continued for a long time, receiving new impulses

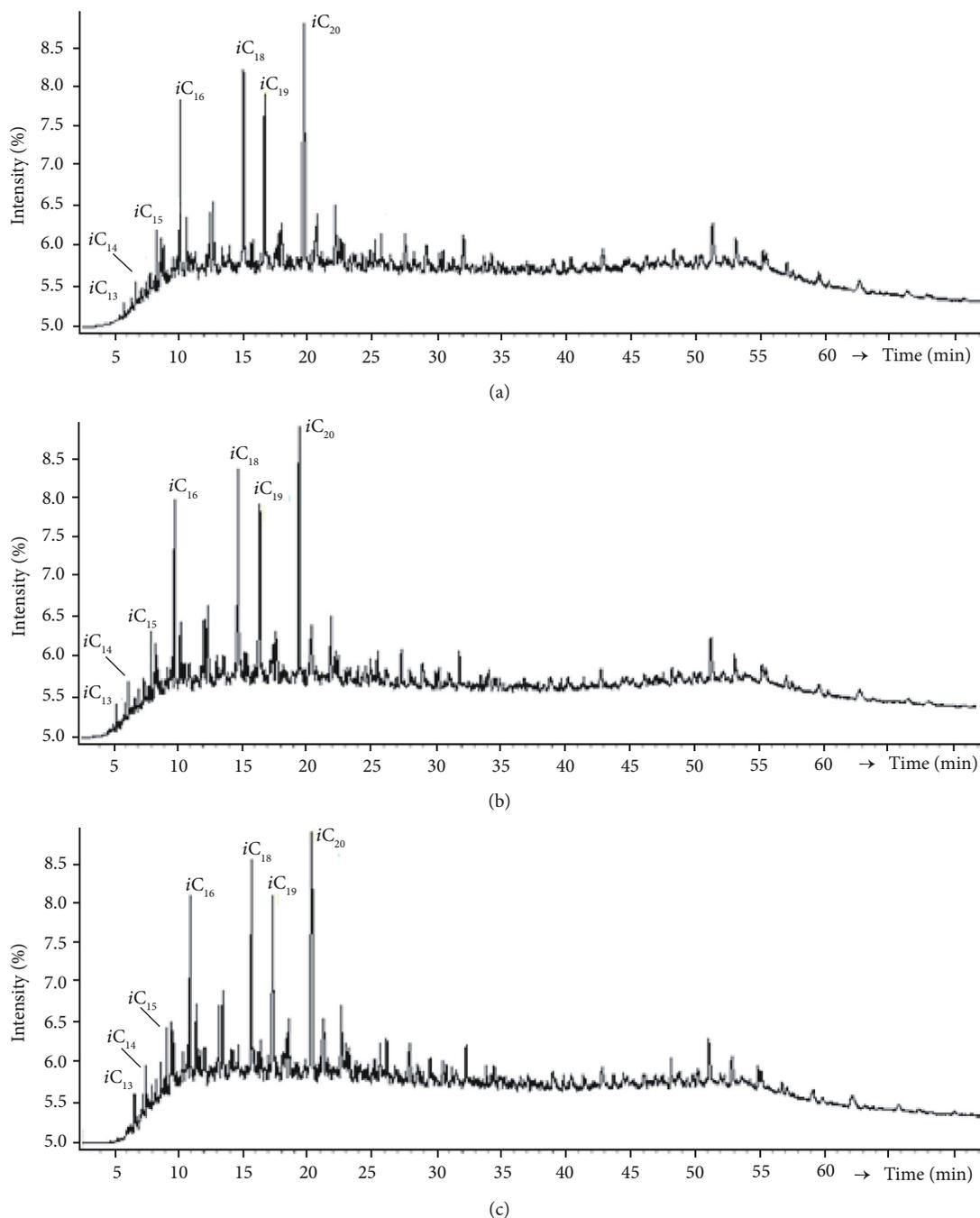


FIGURE 5: GC of saturated fractions of extracts (well 24) depth intervals. (a) 117.5-118.5 m. (b) 121.5-123.5 m. (c) 129-132 m. iC_{13} - iC_{20} : isoprenoid alkane's composition C_{13} - C_{20} .

during periods of activation of the crustal movement, which caused a variety of their composition and properties. The study of extracts from the rocks of the Permian deposits of the Ashal'cha oil field has also been shown that their genesis and composition is related to the nature of the initial migration paraffinic oils and the different influence on their composition of secondary hypergene processes that took place in the territory of their accumulations. n-alkanes are an important classification parameter, since they determine not only the geochemical conditions of the formation of a deposit but also the technological qualities of heavy oils

and, therefore, affect the choice of methods for their extraction and processing.

3.3. The Thermal Effects of the OM Oxidation of Rock Samples from Productive Strata of Permian Deposits Using Differential Scanning Calorimetry. In almost all physical and chemical processes of extraction and processing of hydrocarbons, changes in the amount of heat occur [41-43]. The magnitude of these changes is determined by the properties of the substance and environmental conditions. When the steam-thermal effect on the oil reservoir together with air, the water

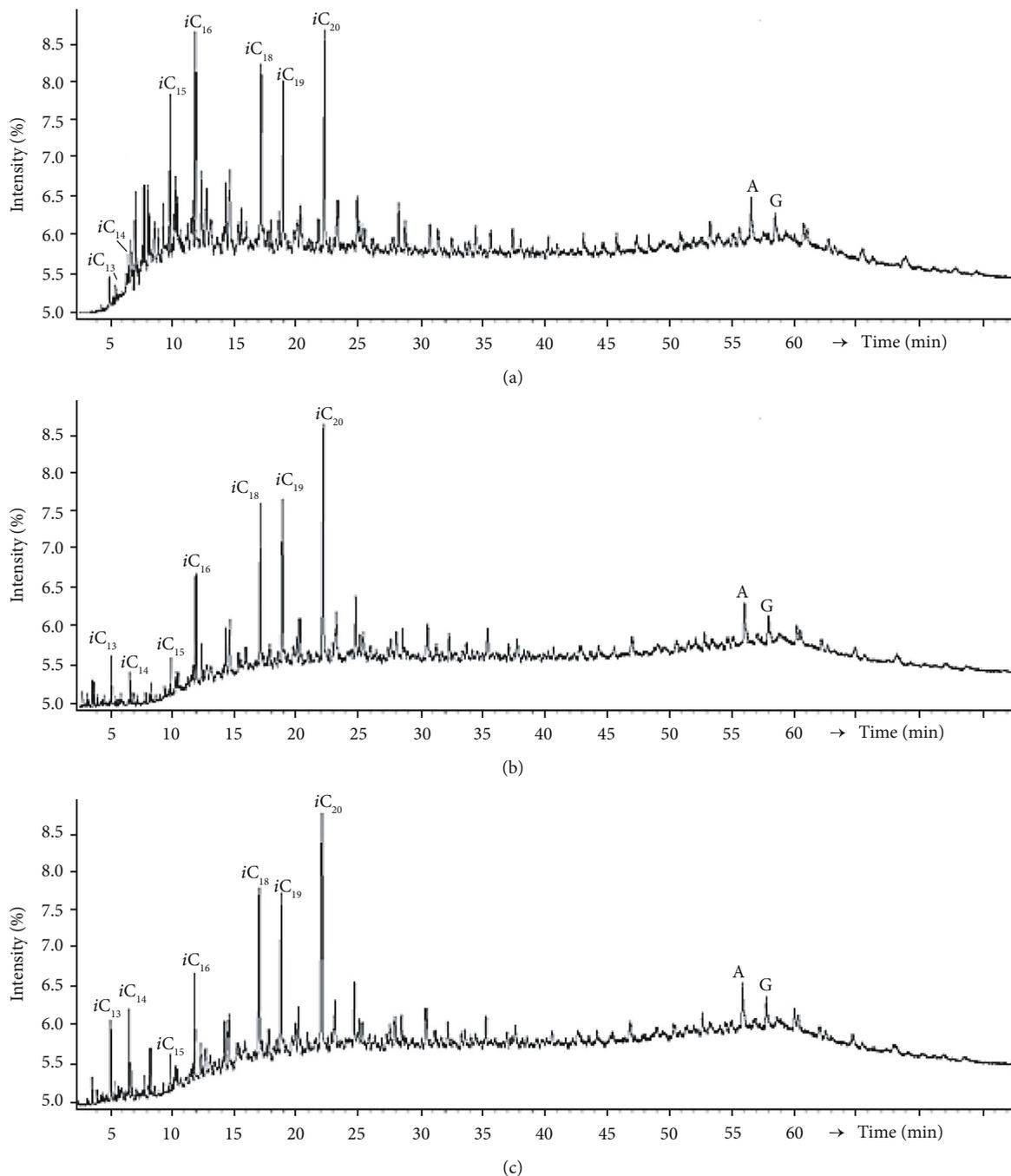


FIGURE 6: GC of saturated fractions of extracts from rock samples (well 9) from the depth interval. (a) 141.6-148.6 m. (b) 148.1-149.7 m. (c) 152.9-154.9 m. iC_{13} - iC_{20} : isoprenoid alkane's composition C_{13} - C_{20} .

injected in certain quantities evaporates and transfers heat to the oil-gas propagation front area as a gas-vapor mixture [3, 12–14, 42]. For the successful implementation of thermal and steam-thermal effects on the formation, it is necessary to know and determine the thermal effects caused by the material composition of the rocks and to be able to determine and select the optimal conditions for the implementation of technological processes of influence on the formation, namely, temperature and pressure. To solve these problems, thermal methods are used, in particular, thermogravimetry and differential scanning calorimetry (TG/DSC) [23, 34, 43–51].

Using the example of oil and bitumen samples that were examined above from the Permian deposits of the Ashal'cha oil field, differing in the mineral composition of rocks, OM content, yields, and group composition of extracts (Table 4), phase transitions were determined using high-pressure differential scanning calorimetry (DSC) [43–45] and the magnitudes of thermal effects resulting from oxidation reactions of various components of OM of oil-containing rocks. The study was carried out in air in the temperature range from 30 to 600°C at a pressure in the reaction system of 5 MPa [47]. Pressure of 5 MPa was used

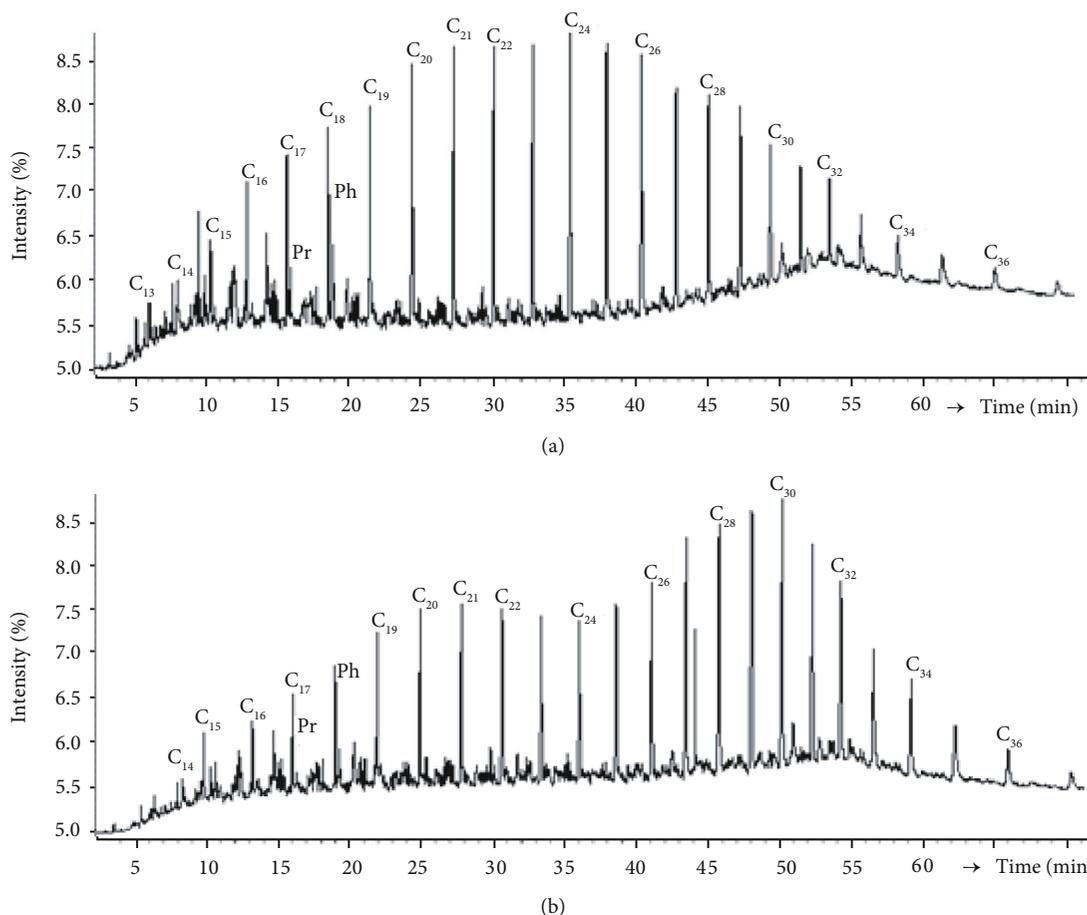


FIGURE 7: GC of saturated fractions of rock extracts (well 106) from the depth interval. (a) 174.4-177.6 m. (b) 187-188.6 m. C₁₃-C₃₆: n-alkanes; Pr: pristane (C₁₉); Ph: phytane (C₂₀).

due to the following factors: firstly, to eliminate the evaporation of crude oil in an unsealed crucible; secondly, to ensure complete oxidation of oil without unburned coke; and thirdly, to simulate the state of the reservoir.

Table 4 shows the area of thermal effects observed in the processes of low-temperature 200-350°C (LTO) and high-temperature 350-500°C (HTO) oxidation of OM of oil-containing rock samples, the maximum inflection temperatures indicating phase transitions in the reaction system with an increase in the temperature of the rock samples, as well as indicators of different abilities of agents of the studied rocks to the manifestation of thermal effects during thermal exposure. This table also shows the onset temperatures of the oxidation process, as well as the parameters associated with the evaporation of water.

Curves of thermal diffusion fluxes of investigated samples of rock made by DSC method are shown in Figures 9 and 10. With the use of the Netzsch Peak Separation software package, DSC curves were decomposed into multiple (separate) peaks.

As a result, a complex picture is observed, which is caused by the multicomponent composition of OM and the composition of free oil found in these rocks. It is difficult to give a specific physical meaning to the “implicit” (small) peaks reflecting thermal effects in both the low-temperature and

high-temperature regions of the DSC curves. The fact is that for different types of oil-saturated rocks with different mineral compositions, the nature of the processes in the low-temperature region (up to 350°C) may differ due to the catalytic effect, which can lead to the emergence of alternative oxidation zones and, therefore, affects the mechanism of the entire oxidation process. Additional, more in-depth studies are needed, showing the effect of individual rock components and minerals on the magnitude of these effects.

On DSC curves of the studied rock samples (Figures 9 and 10), three main areas of manifestation of thermal effects can be identified. According to the literature [43, 45, 47], the first region from 20 to 200°C corresponds to the evaporation of light hydrocarbons and the removal of constitutional water present in clay minerals. The second and third areas in the temperature range of 200-600°C reflect the heat that is released as a result of oxidation reactions of various petroleum components contained in the rock.

The second area of manifestation of thermal effects is observed in the temperature range 200-350°C, which corresponds to the low-temperature oxidation zone 200-350°C (LTO), in which complex processes are observed, including both the formation of free radical particles for further activation of oxidation reactions and the very oxidation process aromatic fractions, as well as the formation of coke. In work

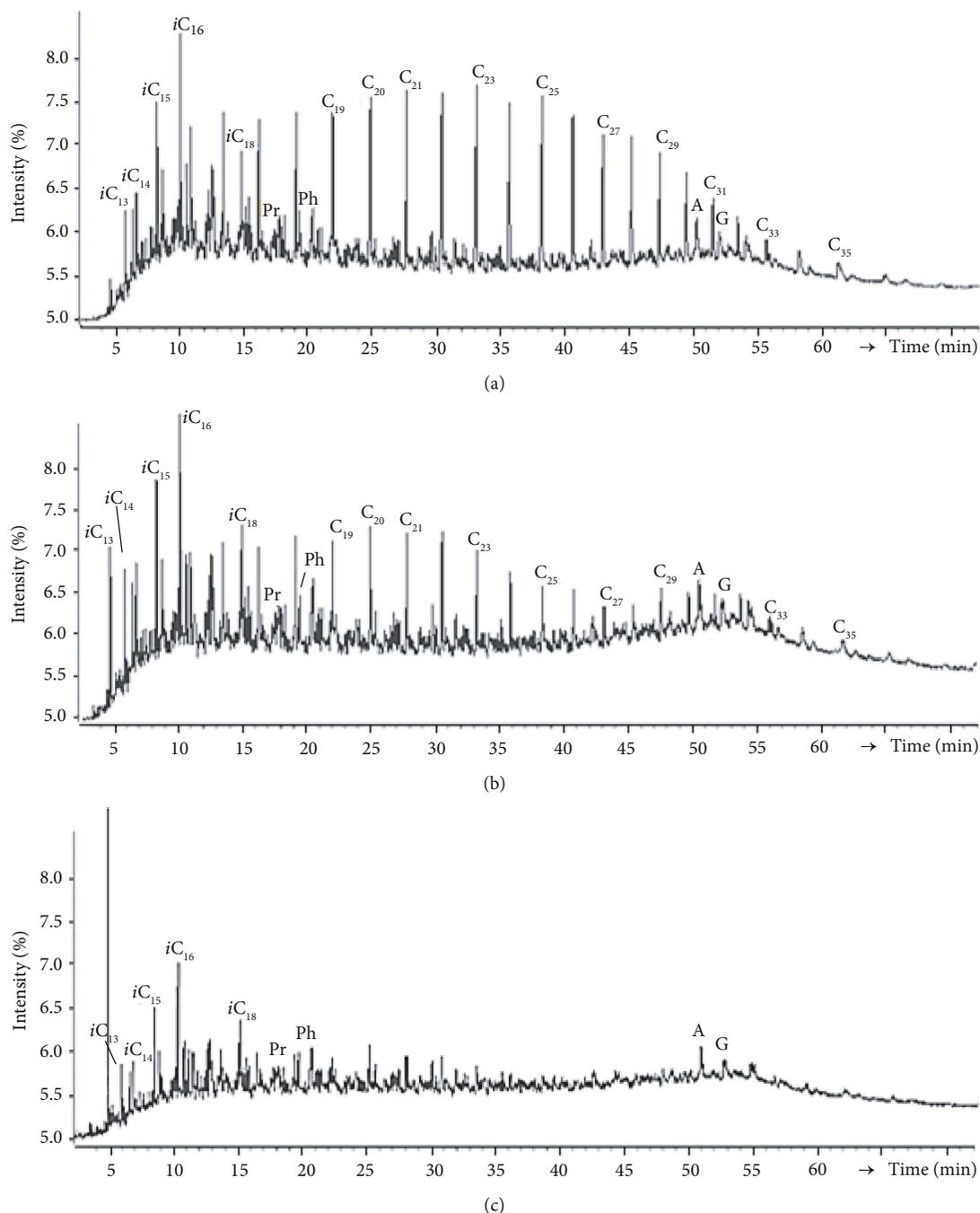


FIGURE 8: GC of saturated fractions of extracts from rock samples (well 107) from the depth interval. (a) 176.5-178 m. (b) 181-182.7 m. (c) 185-187 m. C₁₆-C₃₅: n-alkanes; iC₁₃-iC₁₈: isoprenoid alkane composition C₁₃-C₂₈; Pr: pristane (C₁₉); Ph: phytane (C₂₀); A: adiantan (C₂₉); G: hopan (C₃₀).

[41], it was shown that during thermal transformation of oil components, both intramolecular and intermolecular condensations occur with the formation of resin fraction molecules; the aggregation of which leads to an increase in the yield of asphaltenes. In this case, asphaltenes with short aliphatic chains enter into internal cyclization reactions with the formation of burst structures, which are coke precursors.

The third region of high-temperature oxidation, observed in the temperature range 350-600°C (HTO), is caused by the oxidation of high-molecular structures, such as resins and

asphaltenes, as well as coke formed during the LTO process. The intensity of the peaks on the DSC heat flux curves, as well as the ratio of the thermal effects of the LTO and HTO zones, can provide information about the nature of the oil found in the rock: heavy, extra heavy, medium, etc.

According to the results of experiments, the samples of rocks (1, 2, and 3) from the depth interval 117.5-132 m of well 24 (Table 4, Figure 9) differ most clearly in the magnitude of thermal effects. For samples of rocks 1 and 2, there are two areas of selection of maximum thermal effects:

TABLE 3: Geochemical indicators of saturated fractions of extracts from rocks of the Permian deposits of the Ashal'cha oil field.

Sample no.	Geochemical indicators							
	Pr/Ph	Pr/nC ₁₇	Ph/nC ₁₈	C ₂₇ /C ₁₇	n-(C ₂₇ -C ₃₁)/n-(C ₁₅ -C ₁₉)	2nC ₂₉ /C ₂₈ + C ₃₀	CPI	Ki = Pr + Ph/nC ₁₇ + nC ₁₈
Well 24, depth 117.5-132 m								
1	0.74	8.71	16.67	0.47	0.24	1.53	0.99	12.00
2	0.76	8.72	14.71	0.56	0.19	1.39	0.96	11.34
3	0.78	6.46	9.04	0.58	0.28	1.73	1.02	7.70
Well 9, depth 141.6-154.9 m								
4	0.77	3.92	6.38	0.43	0.41	1.43	1.07	5.01
5	0.69	7.10	17.00	0.30	0.50	1.80	1.18	10.81
6	0.69	9.12	19.00	0.62	0.62	1.40	1.15	13.14
Well 106, depth 174.4-186.6 m								
7	0.75	0.36	0.42	1.26	0.99	1.08	0.99	0.39
8	0.53	0.22	0.34	2.34	2.31	1.01	0.98	0.29
Well 107, depth 176.5-187 m								
9	0.60	0.22	0.35	0.94	0.74	1.03	1.02	0.29
10	0.66	0.36	0.50	0.40	0.39	1.29	0.96	0.43
11	0.68	0.62	1.03	0.24	0.25	1.26	1.07	0.81

200-350°C (S_1) and 350-600°C (S_2) with maximum temperatures at 250 and 400°C, respectively. Thermal effects in the low-temperature range of 20–200°C, indicating evaporation of light free hydrocarbons and removal of water from clay minerals, are present for these samples. For the rock sample 3 from the depth interval of 129-132 m, in contrast to the first two samples from this well, the thermal effects associated with the evaporation of water are not recorded. However, it is noteworthy that the DSC curve of this sample has a significant exothermic effect with a maximum temperature of 156.8°C in the low-temperature region. The process of oil oxidation on this rock has the lowest intensity, due to the low content of OM in it—only 0.92%. This rock sample differs from others in its relatively high content of carbonate minerals (26.84%); the dissociation of which can also be accompanied by thermal effects, as well as the presence of pyrite (3.34%) in it, which has catalytic properties. It is known that oxidation processes may vary depending on the mineral composition of rocks. During the catalytic effect, the oxidation zones (both LTO and HTO) are shifted to lower temperatures due to the formation of active centers and the formation of a transition complex [47]. It can also be assumed that the observed thermal effect in the temperature range of 20–200°C is due to the heat of combustion present in this rock sample, an impurity of modern OM.

In contrast to samples 1 and 2 (Table 4), the obtained data on the beginning of the oxidation process for samples 3, 5, and 7 are in a zone of higher temperatures, which indirectly may indicate the predominance of high-molecular weight components of oil different fractional compositions in the rocks, and also about the possible catalytic effect of rock on the oxidation of petroleum hydrocarbons. Sample 5 from the depth interval 148-149.7 m of well 9 with a higher content of carbonates in the rock (41%) and also relatively low OM content (less than 3%) are characterized by a relatively low total thermal effect. In this rock sample, the

presence of noticeable thermal effects at low temperatures up to 200°C is also noted, which may indicate a low thermal stability of the oil components in the rock, but the influence of the mineral composition of the rocks cannot be excluded. A slightly lower thermal effect with a maximum temperature of 190°C was found for sample 7 (well 106), in the composition of the chemical agents of which n-alkanes are present in noticeable concentrations, and in the mineral composition of the rock, unlike others, there is an admixture of clay minerals.

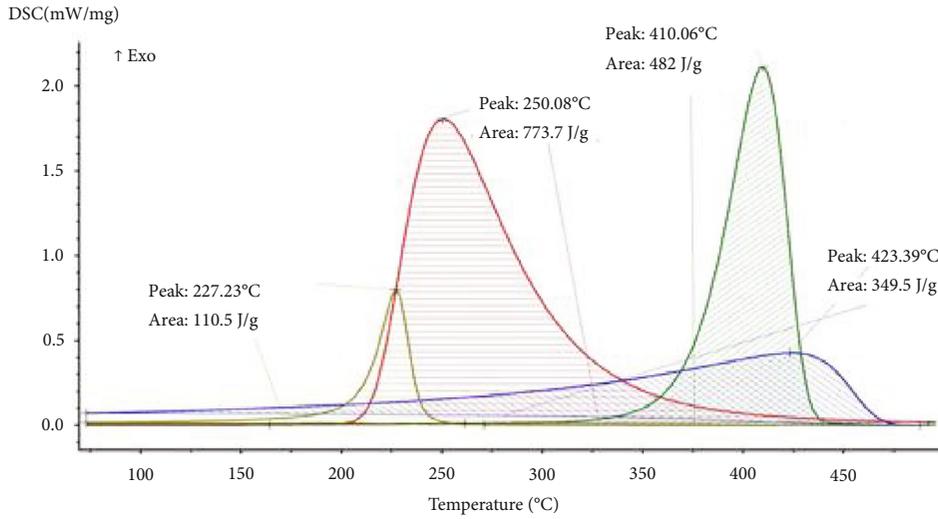
Comparative analysis of the data of calorimetric analysis of rock samples from different sampling intervals, different mineral compositions, and different OM contents shows that the thermal effects of the rocks in LTO and HTO ($\sum S_{1+2}$, J/g) are not related to the content of saturated hydrocarbons, resins, and asphaltenes in the extracts from the rocks. A high correlation with a correlation coefficient of $R^2 = 0.75$ is observed only with the content of aromatic hydrocarbons. There is a correlation dependence with a correlation coefficient of 0.92 between the total thermal effect ($\sum S_{1+2}$, J/g) of rocks and the OM content in rocks (Figure 11(a)), and with a correlation coefficient of 0.80 between the total thermal effect and release of rocks extracts (Figure 11(b)).

It should be noted a high correlation ($R^2 = 0.92$) is traced between the magnitude of the thermal effects manifested in the HTO (Table 4) and the content in the rocks of the high-molecular weight part of the OM that is not extracted by organic solvents, that is, with loss of mass of a rock in the temperature range of 400-600°C according to thermal analysis (Table 1). The correlation dependence between the magnitude of the total thermal effect and the content of calcite in the rocks (Figure 11(c)) is not observed ($R^2 = 0.45$). This suggests that the thermal effects in the high-temperature region are due to the destruction of the high-molecular weight components of the OM, and therefore, to extract them from the rocks, it is necessary to use thermal technologies.

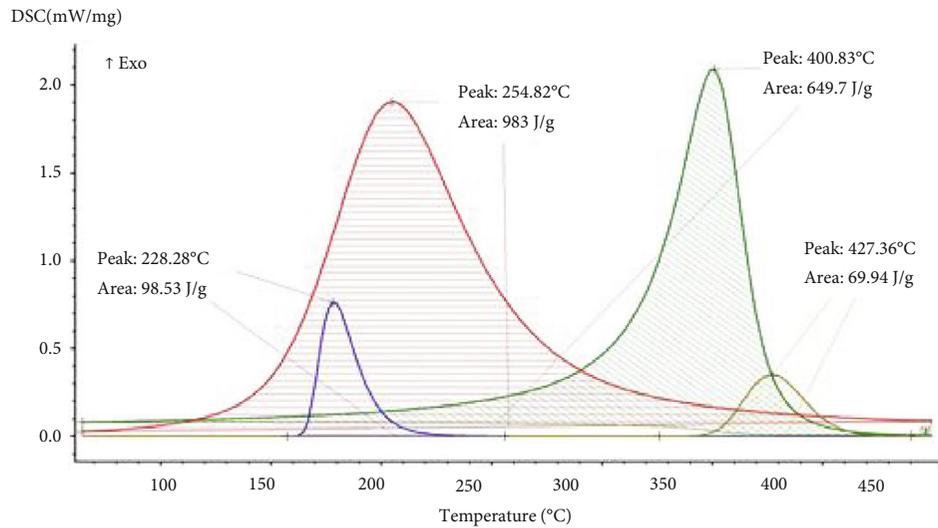
TABLE 4: Thermal analysis data obtained by DSC of rock samples from different interval selections of the Permian sediments of the Ashal'cha oil field.

Sample no.**	Heat effect of water evaporation (J/g)	Water evaporation temperature (°C)	The beginning of the process of oil oxidation (°C)	Low-temperature oxidation (LTO), 200-350°C		High-temperature oxidation (HTO), 350-600°C		Indicator (S ₁ /S ₂)	
				Thermal effect (J/g) (S ₁)	T _{max1} (°C)	Thermal effect (J/g) (S ₂)	T _{max2} (°C)		Thermal effect (J/g) (ΣS ₁₊₂)
Well 24 (117.5-132 m)*									
1	-9.72	129.0	211.4	941.3	250	665.1	410	1606.4	1.41
2	-58.2	119.7	211.9	805.3	254	562.2	400	1367.5	1.43
3	—	—	234.5	111.4	265	62.6	398	174.0	1.78
Well 9 (148.1-149.7 m)									
5	-30.95	104.9	236.1	223.8	264	142.2	402	366.0	1.57
Well 106 (174.4-177.6 m)									
7	-47.83	101.3	227.9	402.5	247	248.2	395	650.7	1.62
Well 107 (181-182.7 m)									
10	—	—	227.5	606.6	252	456.7	415	1063.3	1.33

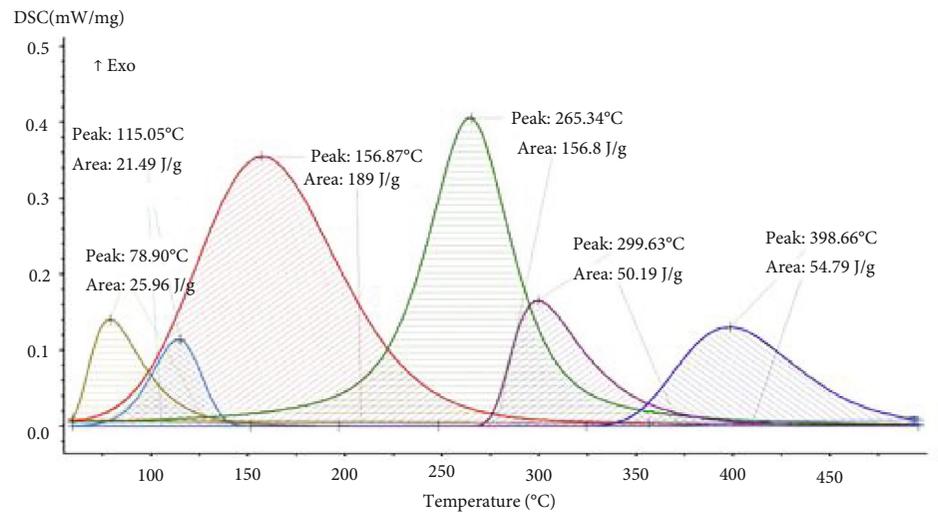
*Sample 1—depth 117.5-118.5 m; sample 2—121-123.5 m; sample 3—129-132 m. **Sample no. See Tables 1, 2, and 3.



(a)



(b)



(c)

FIGURE 9: DSC curves of rock samples from the Permian deposits of the Ashal'cha oil field from the depth intervals of the well 24. (a) 117.5-118.5 m. (b) 121-123.5 m. (c) 129-132 m.

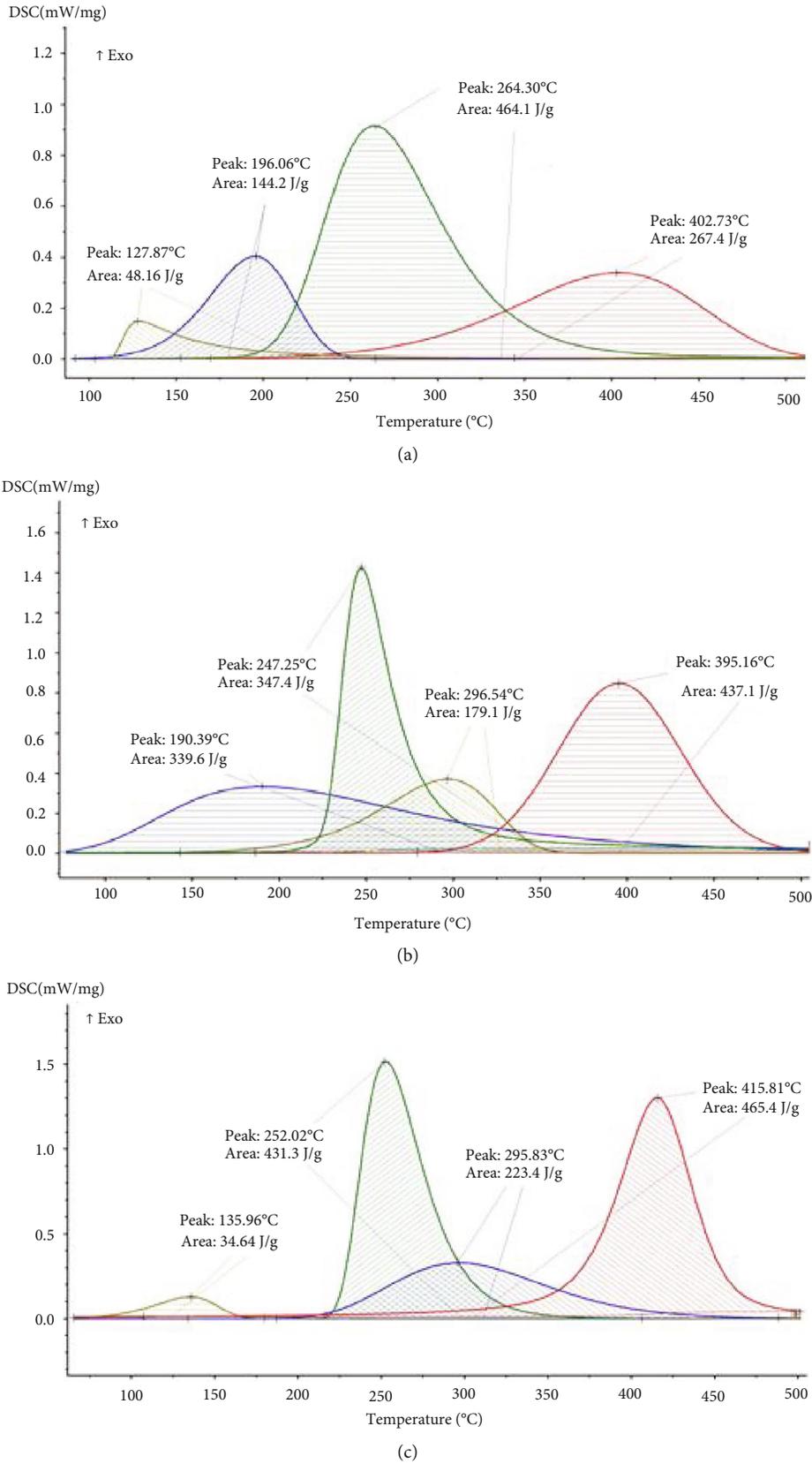


FIGURE 10: DSC curves of rock samples from the Permian deposits of the Ashal'cha oil field from depth intervals of the following wells. (a) Well 9, 148-149.7 m. (b) Well 106, 174.4-177.6 m. (c) Well 107, 181-182.7 m.

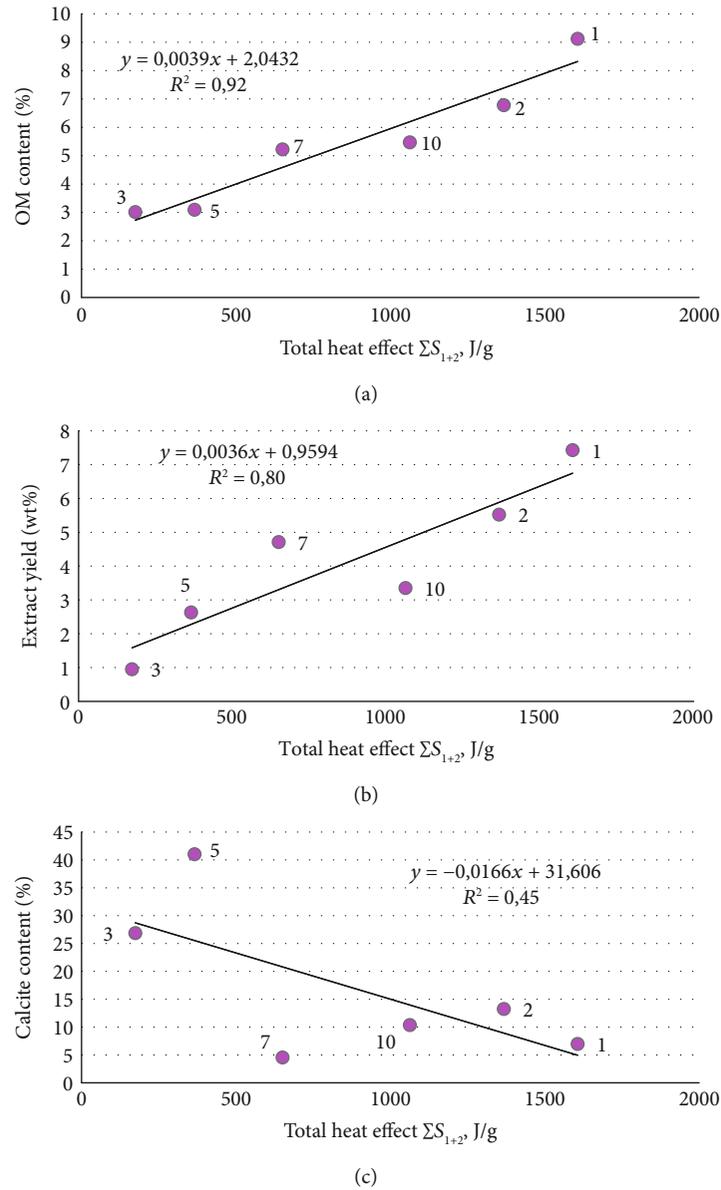


FIGURE 11: Relationships between total heat effect of rocks (ΣS_{1+2} , J/g) and OM content in rocks (a), extracts yield from rocks (b), and calcite content in rocks (c).

High correlation ($R^2 = 0.82$) between indicators S_1/S_2 (Table 4), representing the ratio of the total areas of thermal effects, manifested in the temperature ranges 200–350°C (S_1) and 350–600°C (S_2) and indicator of $F = \Delta m_1(200-400^\circ\text{C})/\Delta m_2(400-600^\circ\text{C})$ of fractional composition of the OM (Figure 12). The studied samples differ from each other that confirms different contributions of their both low-molecular and high-molecular components to the total amount of heat released during thermal exposure of these rocks.

Research results suggest that when applying thermal technologies, oil-bitumen-containing formations with both low and high heat content will be involved in the development. Ultimately, the total thermal effect will allow increasing oil recovery from heterogeneous productive strata of the Permian sediments.

4. Conclusions

In the context of modern methods of converting heavy oils and natural bitumens directly into the oil-bearing rocks, a comprehensive study was conducted of the material composition of oil and bitumen-containing rocks selected from the depth interval of 117.5–188.6 m in the individual wells of the Permian deposits of the Ashal'cha field. It has been established that the rocks from the productive strata of the Permian sediments are heterogeneous in their mineral composition and differ in the composition and content of OM in the rocks, which characterizes their different oil and gas generation potentials. The features of changes in group and hydrocarbon composition of heavy oil, extracted from rocks by organic solvents, depending on the content of OM in them and their mineral composition are revealed. It is

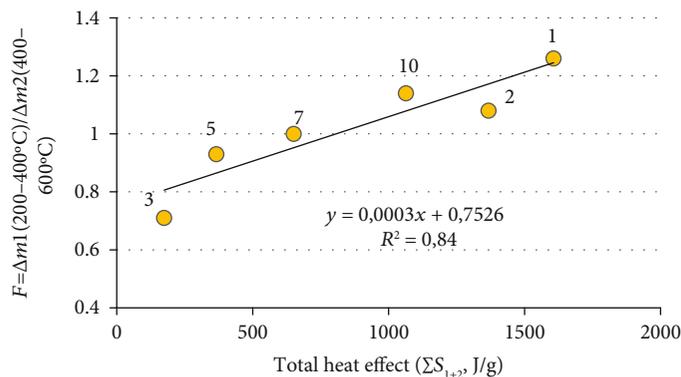


FIGURE 12: Relationship between total heat effect of rocks (ΣS_{1+2} , J/g) and indicator $F = \Delta m_1(200-400^\circ\text{C})/\Delta m_2(400-600^\circ\text{C})$ according to thermal analysis.

shown that with an increase in calcite content in the lower intervals of productive layers, the content of hydrocarbons in rocks decreases and the content of asphaltenes and resins increases in comparison with the composition of fluids of upper oil-saturated intervals enriched in clay and quartz minerals that indicates the occurrence in the zones of their distribution of different intensities of biochemical oxidation processes, leading to an increase in the composition of oil resin and asphaltene components, and so leading to an increase in its viscosity. Using the method of differential scanning calorimetry, it has been shown that when rocks are heated in the range of 20–600°C, exothermic effects of chemical reactions of oxidation of OM in rocks are observed, indicating destructive processes. The investigated rock samples are distinguished by the quantitative characteristics of the thermal effects occurring in the zones of both evaporation of water and light hydrocarbons and low-temperature oxidation (20–350°C) and high-temperature oxidation (350–600°C) of OM. The total thermal effect of the reactions depends on the content, composition, and intensity of thermal transformations of free hydrocarbons contained in the rock, as well as the high-molecular part of OM, which are not extracted from the rocks in full by ordinary extraction. The research results suggest that the residual oil potential of heterogeneous productive strata of the Permian deposits of Tatarstan with different OM contents and types of oil fluids can be successfully implemented using thermal methods that will transform the high-molecular components of the oil into mobile hydrocarbons easily retrievable from the rocks.

Data Availability

All data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

Part 1 of the research (the mineral composition of rocks, thermal analysis, and differential high-pressure scanning calorimetry of rocks) was carried out at Kazan (Volga) Federal University. Part 2 of the work was carried out as in the framework of the state assignment of the FRC of the KazSC RAS.

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