

Article

Evolution of Occurrence States of Retained Hydrocarbons in Organic-Rich Shales During Thermal Maturation: Evidence from Semi-Open System Pyrolysis

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Abstract

Understanding the dynamic evolution of occurrence states of retained hydrocarbons at different thermal maturation stages is crucial for assessing shale oil mobility and enhancing oil recovery. Semi-open pyrolysis experiments were conducted on organic-rich shales from the Chang 7₃ sub-member of the Ordos Basin. Based on semi-open system hydrocarbon generation and expulsion thermal simulation experiments, combined with sequential multi-solvent extraction, gas chromatography–mass spectrometry (GC–MS), Fourier transform infrared spectroscopy (FTIR), and low-temperature N₂ adsorption, this study systematically characterized the composition, occurrence pore size, occurrence state, and quantitative evolution of retained hydrocarbons in organic-rich shales across a maturity range of vitrinite reflectance (Ro) = 0.53–1.59%. The results indicate that maturity significantly influences hydrocarbon generation and pore structure, which in turn affects the occurrence states and contents of retained hydrocarbons. As maturity increases, the contents of various occurrence states reach their peak at around Ro = 0.88%, with free oil predominating at a proportion as high as 86.57%. Beyond Ro = 0.88%, the proportion of free oil decreases rapidly, while the proportions of adsorbed oil, adsorbed–miscible oil, and miscible–adsorbed oil all increase. The content of free oil is not only related to pores in the 20–100 nm range but also to the molecular structure of kerogen. It is proposed that the Ro = 0.74–1.03% stage represents the golden window for free oil yield, with favorable exploration and development potential. These findings provide a theoretical basis for the exploration and development of organic-rich shale oil and the assessment of movable resource potential.

Keywords: group components; occurrence state; retained hydrocarbon; organic-rich shale; shale oil



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1. Introduction

Shale oil resources hold enormous potential and represent a strategic substitute energy source in the petroleum sector [1]. Since the initiation of exploration in 2010, multiple sets

of shale oil source rock intervals have been discovered in China's basins, including the Songliao, Bohai Bay, Ordos, Junggar, and Sichuan basins [2]. However, due to characteristics such as rapid facies changes, low thermal maturity, high clay content, and weak formation drive energy in continental shale oil, exploration and development still face significant challenges in sweet-spot evaluation [3,4]. The occurrence state of shale oil is key to assessing its mobility [5,6]. In recent years, numerous studies have been conducted on the occurrence states and their controlling factors in continental shale oil [7–10]. Previous studies have shown that maturity is one of the main controlling factors of shale oil occurrence. However, the maturities of shale oil in various basins currently differ significantly, and depositional environments and lithologies also vary. Nevertheless, thermal simulation experiments on low-maturity samples can reconstruct the evolution characteristics and occurrence-state evolution patterns of retained oil under the same depositional conditions, which is of great scientific significance for investigating the occurrence states of retained oil at different thermal evolution stages [11].

The occurrence states of shale oil can be classified into three categories: free oil, adsorbed oil, and miscible oil [9,12–14]. Generally, free shale oil is readily flowable, whereas adsorbed and miscible oil are difficult to flow and produce. Therefore, clarifying the content and proportion of shale oil in different occurrence states is of great significance for evaluating movable shale oil resources. Based on differences in occurrence space and molecular polarity, some scholars suggest that free oil is primarily hosted in larger spaces, such as structural fractures, interlayer fractures, microfractures [15,16], and larger inter-crystalline pores and dissolution pores, and is dominated by small-molecule hydrocarbons. Miscible oil is mainly hosted within the internal network structure of kerogen, as well as in asphaltenes and residual water, and is composed predominantly of medium- to small-molecule hydrocarbons. Adsorbed oil is mainly hosted on the internal and external surfaces of the rigid macromolecular framework of kerogen or on the surfaces of rock minerals, and is dominated by medium- to large-molecule hydrocarbons [12,17]. The techniques commonly used for quantitative characterization of shale oil occurrence states mainly include sequential multi-solvent extraction, multi-temperature-step pyrolysis, two-dimensional nuclear magnetic resonance (2D NMR), the kerogen swelling method, and the pre- and post-extraction comparison method [15,18]. Among these, sequential multi-solvent extraction, which takes into account the close relationship between different occurrence states and their hosting spaces, is one of the most widely adopted approaches. In this study, on the basis of the three occurrence states (free, adsorbed, and miscible oil), we further subdivided the miscible oil into two sub-categories—miscible–adsorbed and adsorbed–miscible oil—according to the gradually decreasing oil–rock interaction from the pore wall toward the pore center. Miscible–adsorbed oil refers to hydrocarbons that are predominantly controlled by adsorption on mineral/kerogen surfaces (with relatively high adsorption energy), where some components enter the organic matter network due to polarity and become partially miscible. Adsorbed–miscible oil refers to hydrocarbons that are mainly present as a miscible phase dissolved in organic matter, yet exhibit certain adsorption characteristics due to nanoscale confinement effects or molecular surface polarity. Previous researchers applied multi-solvent stepwise extraction to investigate the occurrence states of mud shale from the Chang 7₃ member in the Ordos Basin and achieved favorable results [13].

Most scholars believe that the occurrence state of shale oil is controlled by multiple factors, including mineral composition, organic matter type and abundance, organic matter maturity, pore structure, and others [9,19]. In addition to the restriction of hydrocarbon molecules by kerogen, the strong adsorption between clay minerals and organic matter at the early stage of thermal evolution also significantly restricts the migration of hydrocarbons, playing an initial retention role [20–22]. Meanwhile, mineral matrices within the

shale (such as pyrite and clay minerals) have a significant catalytic effect on the cracking of aliphatic chains, which can reduce the activation energy of hydrocarbon generation and accelerate the release of hydrocarbon molecules [23]. Previous studies on the shale oil of the Gulong area in the Songliao Basin have investigated the occurrence states at different evolutionary stages and suggested that the hydrocarbon generation of kerogen and the compositional evolution of products exhibit staged characteristics; accordingly, they divided the evolutionary process of the occurrence states of Gulong shale oil into three stages [8].

However, most previous studies have been based on static geological samples from natural evolution, in which the processes of hydrocarbon generation and expulsion are influenced by complex geological factors. Thermal simulation experiments are generally classified into three systems: semi-open, open, and closed. In open and closed systems, fluids are typically collected continuously at the end of the experiment or during the process, whereas in a semi-open system, fluids are expelled only when the pressure reaches a preset value, which more closely resembles episodic hydrocarbon expulsion during natural geological evolution [24]. Moreover, the semi-open system allows for the application of lithostatic pressure and fluid pressure, thereby better replicating subsurface conditions, making it highly suitable for investigating the evolutionary patterns of retained oil occurrence states.

In this study, semi-open system thermal simulation experiments and sequential multi-solvent extraction were employed to accurately characterize the occurrence states and content evolution characteristics of retained oil in the Chang 7₃ sub-member of the Ordos Basin at different thermal maturation stages. The evolution characteristics of group components and n-alkanes were analyzed by group-type fractionation and GC-MS, and the evolution of functional group structures of retained oil was examined using FTIR. In addition, combined with pore structure characterization from N₂ adsorption experiments, the evolution patterns of retained oil occurrence states were analyzed and discussed.

2. Geological Setting

Tectonically, the Ordos Basin is situated on the western margin of the North China Craton and represents a residual basin superimposed on Early–Late Paleozoic large-scale basins, exhibiting characteristics of an intracratonic basin [25]. The Indosinian movement during the Late Triassic, following the collision between the Yangtze and North China blocks, resulted in the formation of a large-scale intramontane depressional lacustrine basin in the Ordos region through basin–range coupling. The Middle–Late Triassic Yanchang Formation depositional period marked the peak developmental stage of the lacustrine basin, characterized by a warm and humid climate and abundant organic matter sources. Its stratigraphy, from bottom to top, can be divided into ten oil-bearing intervals, Chang 10 to Chang 1 [26,27]. Among these, the Chang 7 Member corresponds to the maximum flooding period, with a deep-lake environment hosting flourishing aquatic organisms, giving rise to a set of source rocks dominated by dark mudstones and black shales with a thickness exceeding 100 m (Figure 1a). The Chang 7 Member can be further subdivided into three sub-members (Figure 1b), of which the Chang 7₃ sub-member is the principal source rock, with TOC values ranging from 5% to 25% and Ro values between 0.7% and 1.2%, placing it within the oil window [28]. In previous studies, the Chang 7₃ lacustrine shale oil has been classified lithologically into thick-bedded sandstone type, sandstone interbedded type, and mudstone/shale type; the samples used in this study belong to the mudstone/shale type [7]. Compared with dark mudstone, the black shale of the Chang 7₃ sub-member is characterized by frequent development of multiple types of laminae, high organic matter abundance, good kerogen type, early peak hydrocarbon generation, and high oil content, making it a favorable lithology for shale-type shale oil exploration.

In recent years, risk exploration of shale-type shale oil in the Chang 7₃ sub-member has achieved a breakthrough, with submitted controlled geological reserves of 2.72×10^8 t. The black shale of the Chang 7₃ sub-member exhibits good gas-bearing properties, with an average desorbed gas volume of 1.91 m³/t. These data indicate that the Chang 7₃ sub-member shale is one of the most intensively studied and most representative intervals in continental shale oil exploration in China.

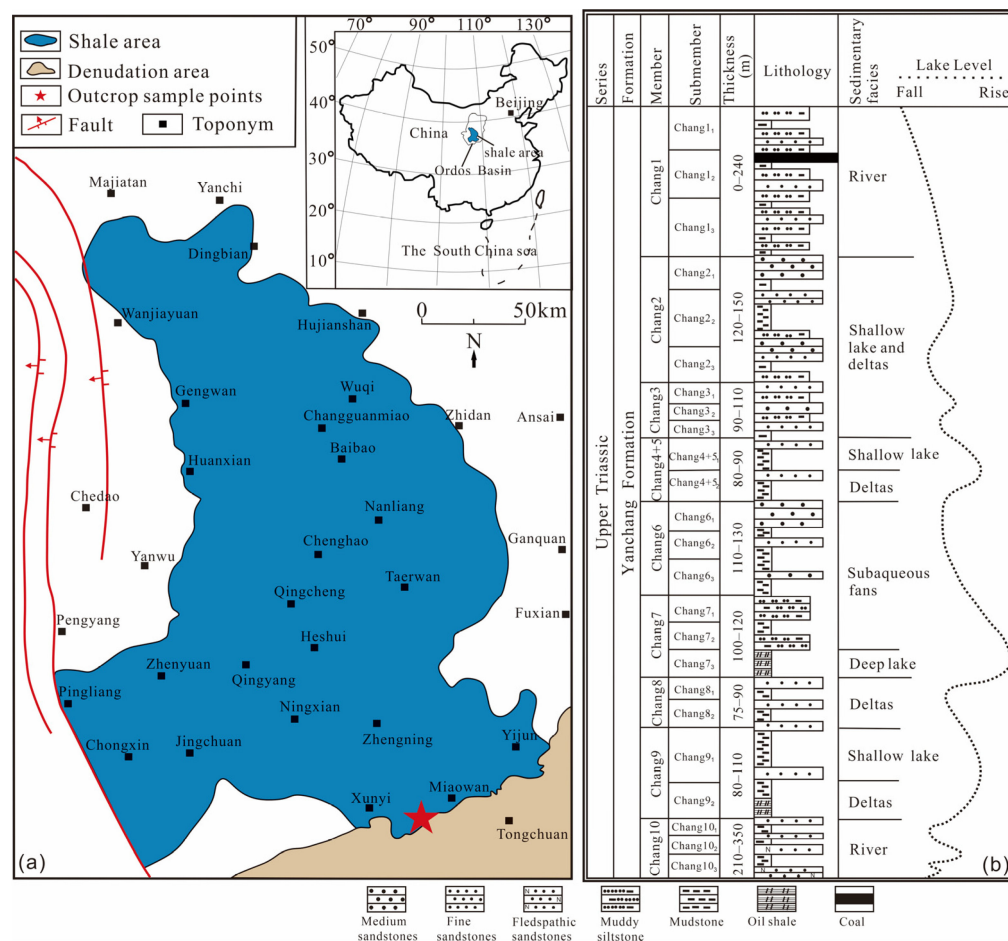


Figure 1. Sampling point in the Ordos Basin (a) and stratigraphic development of the Yanchang Formation (b) (modified from [29]).

3. Materials and Methods

3.1. Samples and Pyrolysis Experiments

The Chang 7₃ sub-member shale is characterized by complex lithology, well-developed laminae, and high total organic carbon content. The shale as a whole is a low-porosity and low-permeability reservoir, with distinct differences in reservoir physical properties under different sedimentary environments. In the Chang 7₃ sub-member, the freshwater-deposited shale mainly develops five types of single laminae: sandy, tuffaceous, organic-rich, argillaceous, and pyritic. These can be classified into five laminae assemblage types: sandy laminae, tuffaceous laminae, sandy mixed laminae, tuffaceous mixed laminae, and organic-rich laminae [26]. The shale samples used for the thermal simulation experiments in this study were collected from the Hejiafang area outcrop in Tongchuan City, Shaanxi Province, Ordos Basin (Figure 1a). The collected samples are low-maturity black shales, predominantly composed of sandy laminae and organic-rich laminae assemblages, with strong heterogeneity. Their geochemical characteristics are shown in Table 1. To better approximate actual geological conditions, eight small cylinders (25 mm in diameter and

40 mm in length) were drilled from the same sample and subjected to thermal simulation experiments at different temperature points.

Table 1. Geochemical parameters of the original sample.

TOC/%	Ro/%	HI (mg/gTOC)	S ₁ (mg/g)	S ₂ (mg/g)	Tmax/°C	Types of Kerogen
18.0054	0.50	711.18	3.34	128.05	429	I

The thermal simulation experiments in this study were conducted using a WYMN-3 high-temperature high-pressure hydrocarbon generation simulator. The WYMN-3 high-temperature and high-pressure simulator is a joint development of the Oil and Gas Research Center (Northwest Institute of Eco-Environment and Resources, CAS) and the Wuxi Research Institute of Petroleum Geology, Jiangsu. This controllable experimental system mainly comprises an autoclave, a cold trap, a gas collector, a hydraulic system, a fluid replenishment system, and a data acquisition system. The system can be regarded as a semi-open high-temperature high-pressure simulation system. In order to compare the occurrence characteristics of retained oil at different temperature points (275 °C, 300 °C, 325 °C, 350 °C, 375 °C, 400 °C, 425 °C, and 450 °C) from the same sample, identical conditions of lithostatic pressure (70 MPa), fluid pressure (32 MPa), and limited hydrocarbon-generation space were applied during the experiments. When sample quantity permitted, we performed 1–2 replicate experiments at each temperature point and repeated the weighing of the experimental results 3–4 times. The final result was taken as the arithmetic mean. In addition, we ensured that the mass balance rate during the experiments remained above 99.5%.

The specific experimental procedure was as follows: during heating, the instrument temperature was first raised at a rate of 10 °C/min until it was 20 °C below the target temperature. After stabilizing at that temperature for 30 min, the temperature was then increased to the target value at a rate of 0.5 °C/min and held at the target temperature for 72 h. The lithostatic pressure was set at 70 MPa and the fluid pressure at 32 MPa. To simulate episodic hydrocarbon expulsion during geological processes, when the system fluid pressure exceeded 34 MPa or dropped below 30 MPa, an electric valve would automatically open to expel hydrocarbons or replenish fluid, thereby maintaining the system pressure at 32 MPa. This cycle continued until the experiment ended after 72 h. Upon completion, liquid hydrocarbons in the collector were washed out with dichloromethane, and then the autoclave and pipeline walls were repeatedly rinsed with dichloromethane to extract the oil remaining on the pipe walls and in the vessel; this portion of oil was defined as expelled oil. The solid residues after thermal simulation were subjected to stepwise extraction using organic solvents, and the soluble organic matter extracted was defined as retained oil. The above procedure was repeated for experiments at each temperature point. For the experimental schematic and more details, please refer to [30].

In this study, vitrinite reflectance measurements were performed on both the original sample and the residual samples from each simulated temperature point. The test was mainly performed using an Axio Scope.A1 microscope and an MSP200 microphotometer, which are from Zeiss (Oberkochen, Germany) and J&M Analytik AG (Essingen, Germany), respectively. For each sample, 25–30 valid measurement points were selected, and the average value was taken as the vitrinite reflectance (Ro) corresponding to that temperature.

3.2. Multi-Solvent Stepwise Extraction

The sequential multi-solvent extraction method employed in this study is based on the principle of “like dissolves like” and the differences in occurrence spaces of shale oil in various occurrence states. Specifically, a combination of solvents with different polarities is used to sequentially extract shale samples of different particle sizes (1 cm × 1 cm × 1 cm, 0.1 cm × 0.1 cm × 0.1 cm, and 80–120 mesh). Free oil occupies relatively large spaces and has strong contact capability with solvents, thus being easily extracted. In contrast, the adsorbed–miscible oil and miscible–adsorbed oil occurring in micropores and enveloped within kerogen macromolecules are difficult to extract due to their limited contact with solvents, and can only be extracted after the bulk samples are manually crushed into small fragments and powders. Furthermore, the hydrocarbon species physically adsorbed and non-covalently chemically adsorbed on mineral surfaces are still difficult to extract even after the samples are crushed into powders, and can only be extracted using strong polar solvents. The detailed experimental procedure is as follows:

Step 1: The sample is crushed into cubes of approximately 1 cm × 1 cm × 1 cm. After weighing, the cubes are placed in a Soxhlet extractor and continuously extracted with a mixture of dichloromethane (DCM) and methanol (93:7 by volume) until the solvent becomes colorless. The extract is then collected in a weighing bottle, air-dried, and weighed. The cumulative weight is recorded as free oil.

Step 2: The blocky sample from Step 1 is crushed into small pieces of about 0.1 cm × 0.1 cm × 0.1 cm. The same solvent mixture (DCM/methanol, 93:7) is used for continuous extraction until the solvent is colorless. The extract is collected, air-dried, and weighed; the cumulative weight is recorded as adsorbed–miscible oil.

Step 3: The small pieces from Step 2 are ground into a powder of 80–120 mesh. Using the same solvent combination and extraction method as in Step 2, continuous extraction is carried out until the solvent is colorless. The extract is collected, air-dried, and weighed; the cumulative weight is recorded as miscible–adsorbed oil.

Step 4: The powdered sample from Step 3 is placed in a Soxhlet extractor and continuously extracted with a mixture of DCM, methanol, and acetone (50:25:25 by volume) until the solvent becomes colorless. The extract is collected, air-dried, and weighed; the cumulative weight is recorded as adsorbed oil.

The residual samples after simulation at each temperature point are subjected to the above experimental procedure. The Soxhlet extractor is heated using a water bath and equipped with a circulating water cooling system, which greatly reduces hydrocarbon loss during the experiment. During weighing, two decimal places are retained, and the average of three measurements is calculated.

3.3. FTIR Analysis

Qualitative and semi-quantitative analysis of the functional group structures of retained oil in the shale samples after thermal simulation was conducted using Fourier transform infrared spectroscopy (FTIR). The experiments were carried out on an ALPHA I FTIR spectrometer manufactured by Bruker Corporation (Bremen, Germany). Sample preparation was performed using the conventional potassium bromide (KBr) pellet method, with the spectral resolution set to 4 cm^{−1} and the scanning range covering 4000–400 cm^{−1}.

Based on previous studies, the infrared spectra were primarily divided into two spectral regions (2800–3000 cm^{−1} and 1570–1670 cm^{−1}), and peak fitting was performed using OMNIC 9.7 and PeakFit 4.12 software, as shown in Figures 2 and 3. The corresponding absorption peak assignments are listed in Table 2.

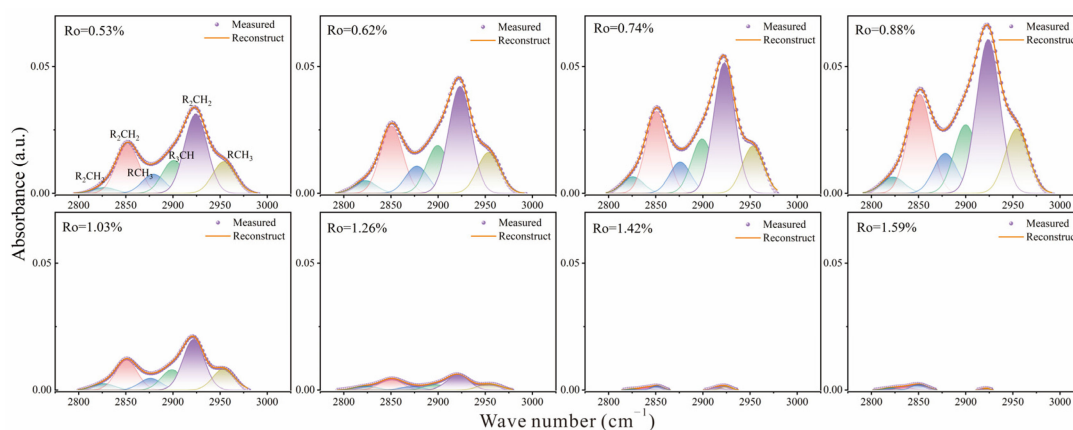


Figure 2. Peak fitting characteristics of aliphatic in 2800–3000 cm^{-1} .

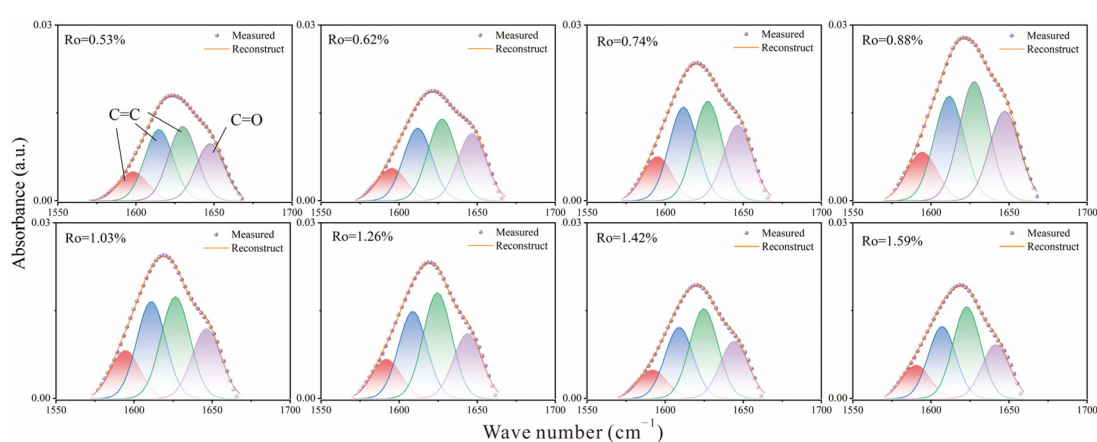


Figure 3. Peak fitting characteristics of aromatic in 1570–1670 cm^{-1} .

Table 2. Assignment of FTIR absorption peaks for organic compounds.

Peak Center (cm^{-1})	Assignments
2954	asymmetric $-\text{CH}_3$ stretching
2923	asymmetric $-\text{CH}_2-$ stretching
2900	aliphatic C–H stretching
2877	symmetric $-\text{CH}_3$ stretching
2850	symmetric $-\text{CH}_2-$ stretching
2822	symmetric $-\text{CH}_2-$ stretching
1646	secondary amides C=O stretching
1626	aromatic C=C stretching
1611	aromatic C=C stretching
1595	aromatic C=C stretching

To further characterize the details and trends of functional group structures of retained oil during thermal evolution, several quantitative indices were calculated (Figure 4, including the $-\text{CH}_3/-\text{CH}_2$ ratio and the aliphatic index (A-factor). The aliphatic index (A-factor) is calculated as $[I_{2850} + I_{2923}]/[I_{2850} + I_{2923} + I_{1611}]$, reflecting the abundance of aliphatic groups relative to aromatic groups, while the $-\text{CH}_3/-\text{CH}_2$ ratio, calculated as I_{2954}/I_{2923} , reflects the length and degree of branching of aliphatic side chains (where I represents the peak area at the corresponding wavenumber) [30–32].

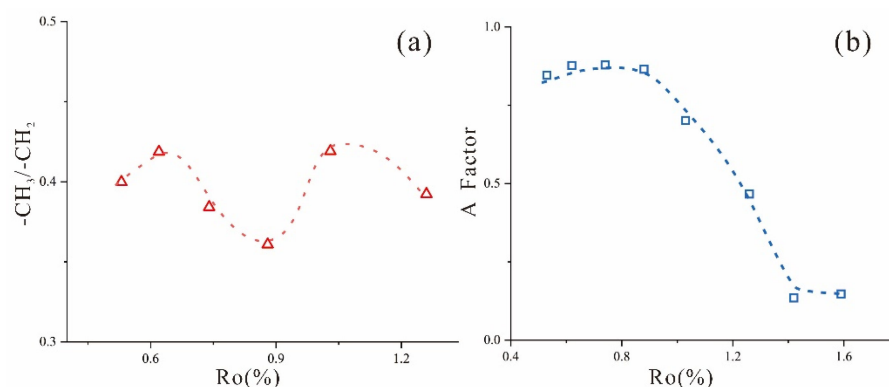


Figure 4. Evolution characteristics of aliphatic structural parameters: (a) for $-CH_3/-CH_2$ ratio and (b) for A-Factor.

3.4. Low Temperature N_2 Adsorption

The low-temperature N_2 adsorption experiments in this study were performed using an ASAP 2020 V4.02 instrument manufactured by Micromeritics (Norcross, GA, USA). In the experiment, approximately 0.25 g of extracted powder samples (60–80 mesh) were vacuum-dried at 110 °C for 12 h to remove moisture and volatile components, and then subjected to testing and analysis. The pore size range covered was 1.7–300 nm, including mesopores as well as some micropores and macropores. The specific surface area was calculated using the BET model, the pore-size distribution was calculated using the BJH model, and the pore volume was calculated using the DFT model.

4. Results

4.1. Characteristics of Hydrocarbon Generation, Expulsion, and Retention Evolution in Organic-Rich Shales

Based on semi-open system thermal simulation experiments on shale samples from the Chang 7₃ sub-member of the Ordos Basin, the evolution characteristics of oil generation, expulsion, and retention in the shale were quantitatively characterized, with results presented in Figure 5. Overall, with increasing simulation temperature, the oil generation process exhibits distinct staged features, and the yields of all liquid hydrocarbons show a trend of first increasing and then decreasing. According to the evolutionary trend of total liquid hydrocarbons (the sum of expelled oil and retained oil), the oil generation process of the shale samples can be divided into the following three main stages:

1. Early accumulation stage ($Ro = 0.53$ – 0.62%): At this stage, kerogen has just entered the oil generation threshold. The total liquid hydrocarbon yield increases slowly, while the expelled oil yield is extremely low (2.07–14.89 mg/g TOC).
2. Major oil generation stage ($Ro = 0.62$ – 0.88%): With increasing maturity, kerogen undergoes large-scale thermal degradation. The total liquid hydrocarbon yield reaches its peak (531.47 mg/g TOC) at around $Ro = 0.88\%$, while the retained oil yield simultaneously reaches its maximum (478.68 mg/g TOC). At this point, the expelled oil gradually reaches its peak (156.04 mg/g TOC).
3. Gas generation by cracking stage ($Ro = 0.88$ – 1.59%): When maturity reaches $Ro = 1.26\%$, the generated liquid hydrocarbons undergo extensive secondary cracking, resulting in a rapid decline in both total liquid hydrocarbon and the retained oil yields.

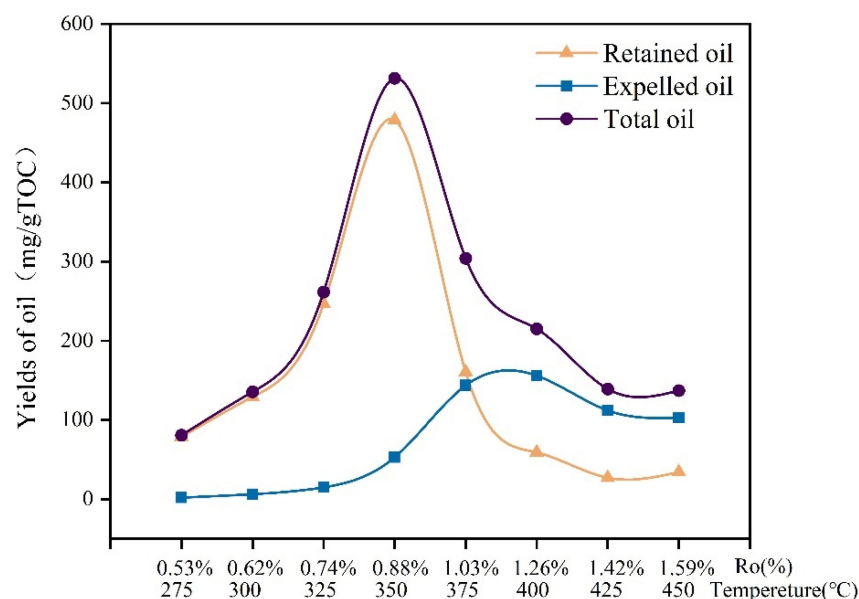


Figure 5. Yield characteristics of expelled oil, retained oil, and total oil.

4.2. Yield Characteristics of Shale Oil in Different Occurrence States

By performing sequential multi-solvent extraction on the residual samples after thermal simulation, the content evolution characteristics of four occurrence states of retained oil—free oil, adsorbed–miscible oil, miscible–adsorbed oil, and adsorbed oil—were quantitatively characterized (Figure 6). The experimental results show that the yields of all occurrence states generally exhibit a trend of first increasing and then decreasing with increasing maturity, primarily reaching their peak values at around $Ro = 0.88\%$.

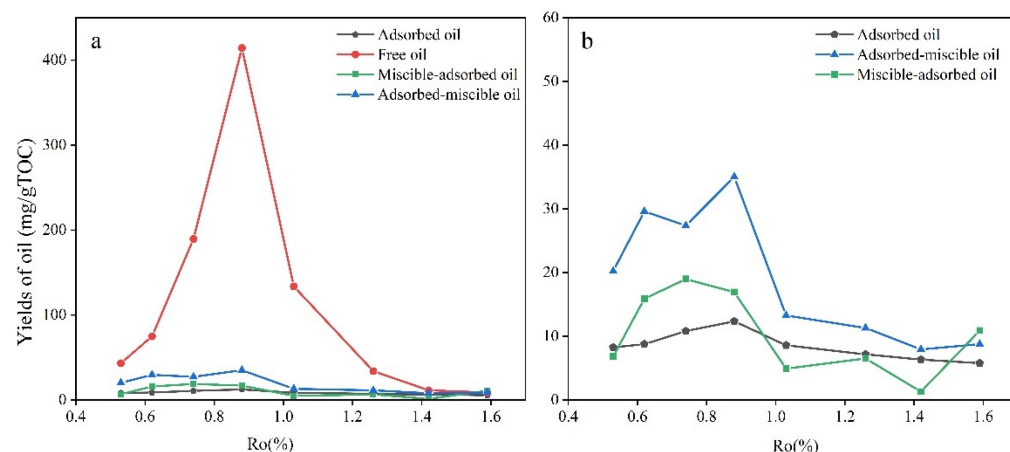


Figure 6. Yield characteristics of various occurrence states: free oil, adsorbed–miscible oil, miscible–adsorbed oil, and adsorbed oil. (a) represents the overall characteristics of free oil, adsorbed–dissolved oil, dissolved–adsorbed oil, and adsorbed oil. (b) magnifies the details of adsorbed–dissolved oil, dissolved–adsorbed oil, and adsorbed oil.

According to the evolutionary trends of yields for each occurrence state, the evolution process can be divided into the following three stages:

1. $Ro = 0.53\text{--}0.62\%$: At this stage, the yield of free oil is relatively low, reaching only 74.94 mg/g TOC at $Ro = 0.62\%$. The yields of the other occurrence states are also low during this stage;
2. $Ro = 0.62\text{--}0.88\%$: The yield of free oil increases substantially, rising from 189.6 mg/g TOC at $Ro = 0.74\%$ to 414.37 mg/g TOC at $Ro = 0.88\%$, becoming the dominant

component of retained oil. Meanwhile, adsorbed–miscible oil, miscible–adsorbed oil, and adsorbed oil also reach their peak values during this stage;

3. $R_o = 0.88$ – 1.59% : In this stage, affected by secondary cracking of liquid hydrocarbons, the yields of all occurrence states show a rapidly decreasing trend. At $R_o = 1.59\%$, free oil decreases to 8.85 mg/g TOC , and the other occurrence states also shrink correspondingly.

4.3. Geochemical Characteristics of Free Oil

Through group-type fractionation and GC-MS analysis of saturated hydrocarbons in free oil at each thermal simulation temperature point, the evolutionary trends in hydrocarbon composition and molecular structure of free oil during thermal maturation were revealed. In terms of group-type composition evolution, with increasing thermal maturity, free oil exhibits increasing proportions of saturated hydrocarbons and aromatic hydrocarbons, while the proportions of non-hydrocarbons and asphaltenes decrease (as shown in Figure 7). In the $R_o = 0.53$ – 0.88% range, saturated and aromatic hydrocarbons first show a slight decrease and then an increasing trend, with saturated hydrocarbons exhibiting a more pronounced variation, while aromatic hydrocarbons show relatively minor changes. In the $R_o = 0.88$ – 1.59% range, as liquid hydrocarbons undergo extensive cracking, saturated and aromatic hydrocarbons gradually become dominant. Overall, the proportions of non-hydrocarbons and asphaltenes decrease, though the asphaltene proportion shows a slight increase within the $R_o = 0.53$ – 0.88% stage.

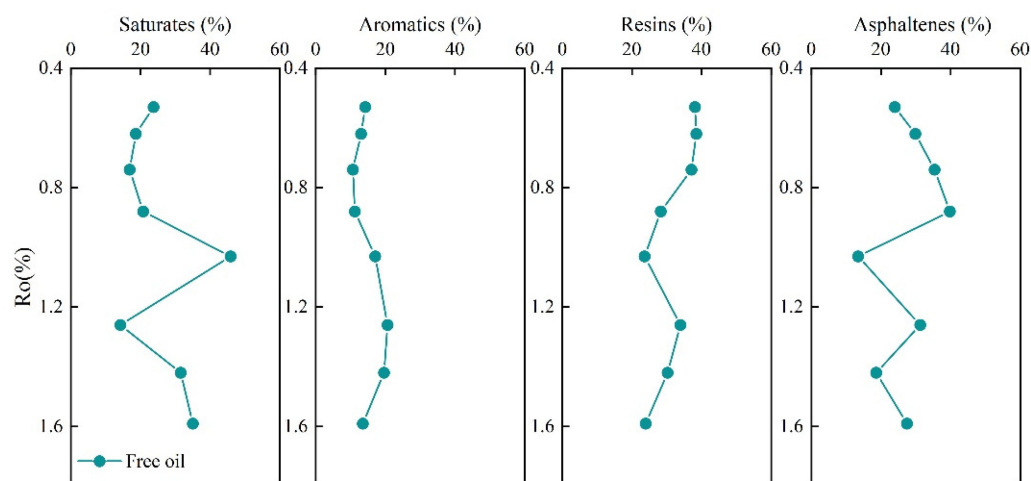


Figure 7. Proportions of group compositions in free oil.

The carbon number distribution of saturated hydrocarbons in free oil is shown in Figure 8, mainly ranging from nC_{13} to nC_{33} and displaying a unimodal pattern overall. At $R_o = 0.53\%$, the main peak carbon is nC_{18} ; within $R_o = 0.63$ – 1.26% , the main peak carbon stabilizes at nC_{17} , indicating a shift toward lower carbon numbers. However, when maturity exceeds $R_o = 1.26\%$, the main peak carbon shifts notably toward higher carbon numbers. The evolution of the light-to-heavy ratio of n-alkanes in free oil ($\Sigma nC_{21-} / \Sigma nC_{22+}$) is presented in Figure 9, showing a distinct staged trend. At $R_o < 1.26\%$, lower-carbon-number alkanes are clearly predominant, whereas after $R_o > 1.26\%$, higher-carbon-number alkanes become more dominant.

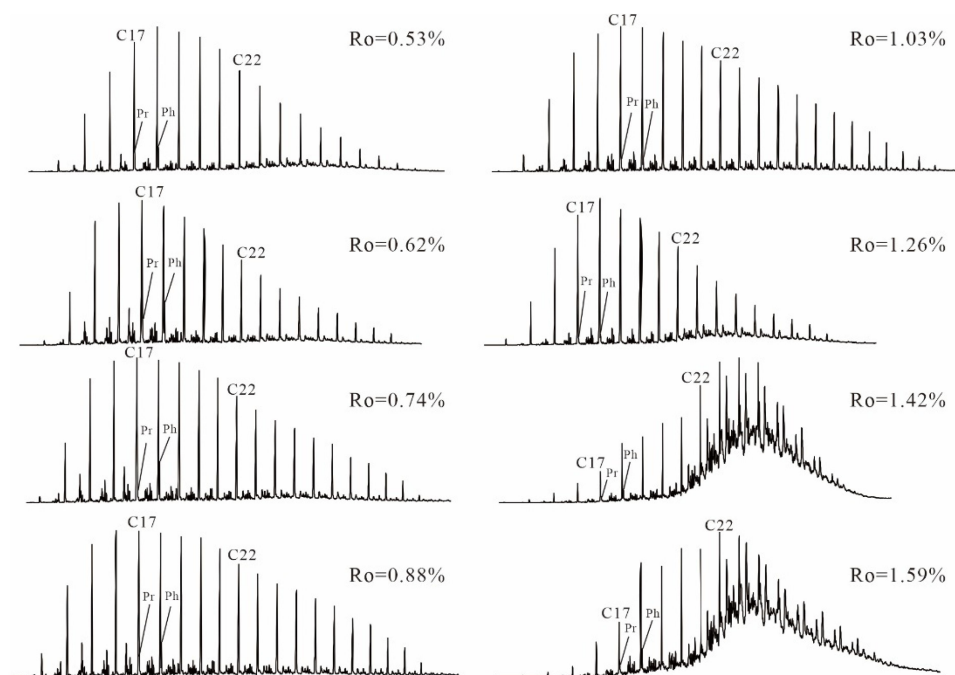


Figure 8. Carbon-number distribution of saturated hydrocarbons in free oil.

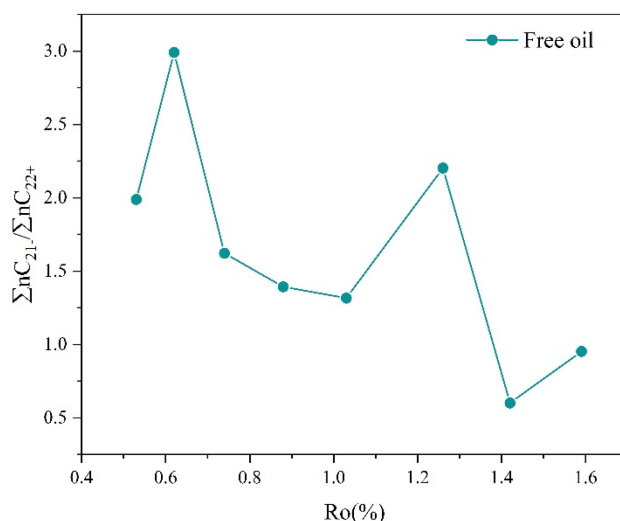


Figure 9. Characteristics of the light-to-heavy n-alkane ratio ($\Sigma nC_{21-} / \Sigma nC_{22+}$).

4.4. FTIR Characteristics of Retained Oil

Through FTIR experiments on retained oil, the dynamic evolution patterns of functional groups in retained oil with increasing maturity were systematically characterized. As shown in Figures 2 and 3, in the $Ro = 0.53\text{--}0.88\%$ range, the spectra are characterized by strong aliphatic C–Hx stretching vibration peaks ($2800\text{--}3000\text{ cm}^{-1}$), with distinct absorption peaks at 2923 cm^{-1} (asymmetric $-\text{CH}_2-$ stretching), 2850 cm^{-1} (symmetric $-\text{CH}_2-$ stretching), and around 1600 cm^{-1} (C=C stretching vibration), while the absorption peak at 1700 cm^{-1} (C=O stretching) is almost indistinguishable. This reflects the structural attributes of Type I kerogen, which is rich in long-chain alkanes and polycyclic aromatic structures, with very few oxygen-containing functional groups. As maturity increases to the $Ro = 0.88\text{--}1.59\%$ range, the intensities of these aliphatic absorption peaks decrease dramatically (Figure 2), indicating that the retained oil has undergone extensive detachment of aliphatic side chains. The relative intensity of the C=C stretching vibration peak (around

1600 cm^{-1}), representing the aromatic ring skeleton, gradually increases with maturity and then stabilizes, with a slight decreasing trend (Figure 3).

With increasing maturity, the $-\text{CH}_3/-\text{CH}_2$ ratio exhibits a trend of first decreasing, then increasing, and finally decreasing again as maturity rises (Figure 4a). In addition, the A-factor shows a clear decreasing trend, especially after $\text{Ro} = 0.74\text{--}0.88\%$, where it drops significantly from 0.87 to 0.70 (Figure 4b).

4.5. Characteristics of Pore Structure

The pore structure of the extracted samples was tested and characterized by low-temperature nitrogen adsorption experiments, with the results shown in Figures 10 and 11. According to the pore size classification scheme of the International Union of Pure and Applied Chemistry (IUPAC), pores can be divided into micropores (<2 nm), mesopores (2–50 nm), and macropores (>50 nm). The low-temperature nitrogen adsorption–desorption isotherm curves are presented in Figure 10. The curves exhibit an S-shape, consistent with Type II isotherm characteristics, and display distinct hysteresis loops that correspond to H3 and H4 types. These features indicate that the shale samples have well-developed pores, including micropores, mesopores, and macropores, with pore morphologies such as plate-like slits, microfractures, and wedge-shaped pores.

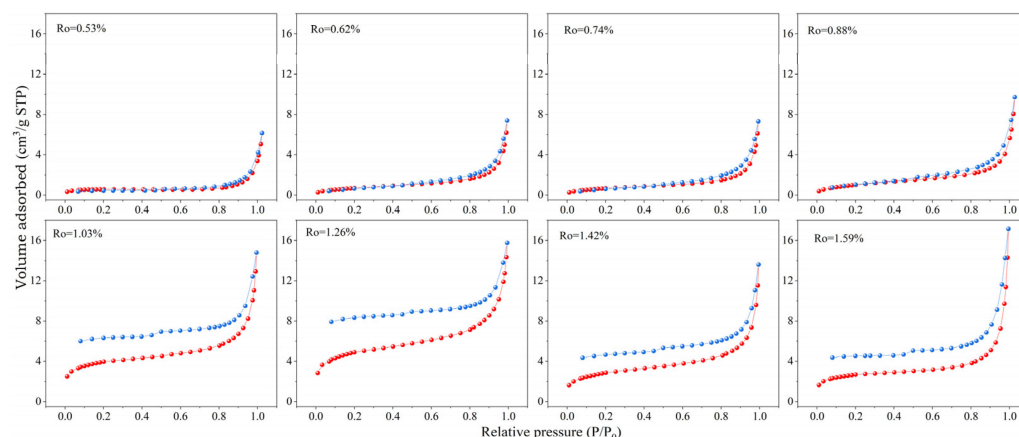


Figure 10. Characteristics of nitrogen adsorption–desorption curves at various maturity levels.

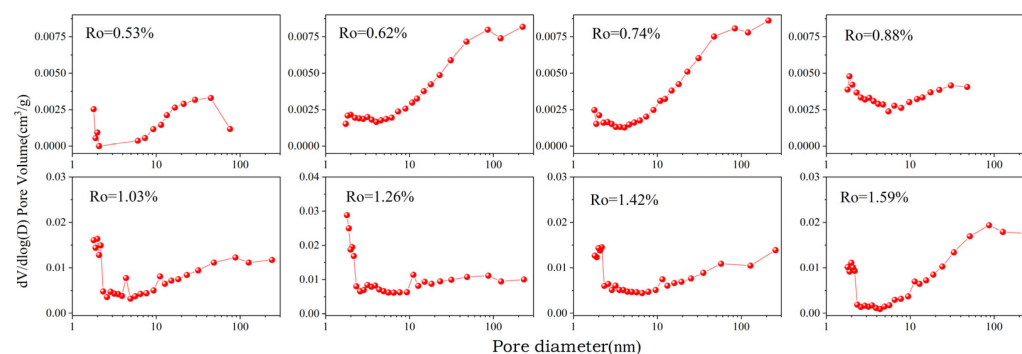


Figure 11. Pore-size distribution characteristics under different maturity levels.

The BJH pore-size distribution characteristics of shale samples at different thermal simulation temperatures are shown in Figure 11. At $\text{Ro} = 0.53\%$, the shale is close to the original sample pore structure, with micropores, mesopores, and macropores all being developed, and the main pore contribution comes from mesopores and macropores in the 10–100 nm range. In the $\text{Ro} = 0.62\text{--}0.74\%$ stage, kerogen undergoes cracking to generate oil, leading to extensive development of mesopores around 100 nm and an overall increase in

pore volume. At $R_o = 0.88\%$, the oil generation peak is reached, with a large number of pores in the 2–10 nm range developing, the total pore volume increasing rapidly, and the nitrogen adsorption capacity increasing notably. In the $R_o = 1.03$ – 1.42% stage, the overall pore volume continues to increase, with relatively minor differences in pore contribution across the 2 nm–100 nm range, and a peak observed around 10 nm. At $R_o = 1.59\%$, the pore development is similar to that of the previous stage, but macropores around 100 nm are extensively developed and make the dominant contribution.

The pore volume and specific surface area characteristics at different stages are summarized in Table 3. As shown, the total pore volume generally exhibits an increasing trend, with a rapid increase after reaching the oil generation peak. The specific surface area is relatively low at low maturity stages; it increases rapidly after the oil generation peak and then decreases sharply after $R_o = 1.26\%$. The BJH pore volume and micropore volume show similar trends—both increase rapidly after the oil generation peak, but their growth rates slow down after $R_o = 1.26\%$.

Table 3. Pore structure parameters under different maturity levels.

$R_o/\%$	BET Specific Surface Area (m^2/g)	Total Pore Volume (cm^3/g)	Micropore Volume (cm^3/g)	BJH Pore Volume (cm^3/g)
0.53	1.7102	0.00953	0.000566	0.00476
0.62	2.6231	0.011423	0.000197	0.01120
0.74	2.4941	0.011308	0.000090	0.01110
0.88	3.8952	0.01505	0.000652	0.00591
1.03	12.7003	0.02289	0.00239	0.0203
1.26	15.9947	0.02440	0.00233	0.02188
1.42	9.5791	0.02104	0.000757	0.02016
1.59	8.5683	0.02652	0.00157	0.02485

5. Discussion

5.1. Occurrence States Evolution of Organic-Rich Shale Oil

Based on the sequential multi-solvent extraction method, the proportions and yields of shale oil in different occurrence states during thermal evolution were characterized, and the functional group structural characteristics of the retained oil were revealed using infrared spectroscopy. Based on these findings, combined with the compositional characteristics of saturated hydrocarbons in free oil, we can gain a better understanding of the occurrence features of retained oil, as well as the carbon number distribution and molecular structural changes in components throughout the entire thermal evolution process.

In the first stage ($R_o = 0.53$ – 0.74%), kerogen undergoes initial cracking, mainly generating macromolecular components such as asphaltenes and non-hydrocarbons. The retained oil yield is higher than that of expelled oil. Free oil is relatively abundant, and its proportion gradually increases, while the contents and proportions of adsorbed–miscible oil, miscible–adsorbed oil, and adsorbed oil remain low and show a decreasing trend. The saturated hydrocarbons in free oil are mainly distributed in the range of nC_{13} to nC_{31} , with the main peak at nC_{18} , exhibiting a clear predominance of lower-carbon-number alkanes (Figure 8). The proportion of asphaltenes and non-hydrocarbons reaches 62% and increases gradually (Figure 12). The aliphatic branching index ($-\text{CH}_3/-\text{CH}_2$ ratio) shows a slight increase, followed by a decrease, reflecting the initial cleavage of branched chains at the ends of long-chain alkyl side chains and the generation of abundant methyl groups ($-\text{CH}_3$). However, after maturity exceeds $R_o = 0.62\%$, kerogen enters the main hydrocarbon-generation stage, where C–C single bonds begin to break, releasing large amounts of long-chain alkanes from the kerogen macromolecular structure. As a result, the

yield of methylene groups surpasses that of methyl groups. The concomitant increase in the aliphatic A-factor confirms the substantial generation of aliphatic compounds.

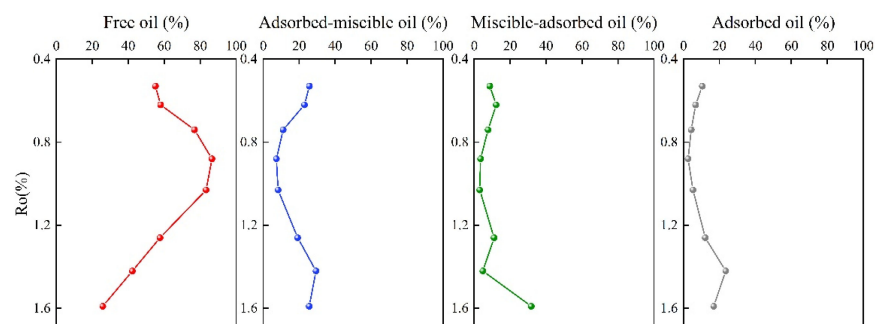


Figure 12. Evolution characteristics of proportions under different occurrence states.

In the second stage ($R_o = 0.74\text{--}1.03\%$), shale oil reaches its peak oil generation period. The retained oil yield surges to a maximum of 478.68 mg/g TOC. Asphaltenes and non-hydrocarbons begin to crack into alkanes of various carbon numbers, while long-chain alkanes and cyclic structures further break down, generating alkanes and alkenes with different chain lengths. Owing to the shortening of long-chain alkanes, which facilitates their expulsion, the content and proportion of the expelled oil increase. Meanwhile, because short-chain alkanes are weakly polar, they tend to occur as free oil in larger pores [20], leading to a sharp increase in free oil yield as well. The contents of adsorbed–miscible oil, miscible–adsorbed oil, and adsorbed oil also reach their maximum values at around $R_o = 0.88\%$. The carbon number distribution of free oil ranges from nC_{13} to nC_{34} , with the main peak at $nC_{16}\text{--}nC_{17}$, and the predominance of lower-carbon-number alkanes gradually weakens (Figure 8). The $-\text{CH}_3/-\text{CH}_2$ ratio drops to its lowest value at $R_o = 0.88\%$ (Figure 4a), indicating that at this maturity, the yield of long-chain alkanes generated from kerogen cracking reaches its peak, accompanied by a sharp increase in methylene content. Beyond this maturity, the aliphatic intensity declines rapidly, suggesting extensive cleavage of long-chain alkanes after $R_o = 0.88\%$. The continuous decrease in the A-factor is not only related to alkane cracking and expulsion but also associated with the aromatization of aliphatic structures.

In the third stage ($R_o = 1.03\text{--}1.59\%$), the proportions of asphaltenes and non-hydrocarbons in free oil gradually decrease to their lowest levels, while aromatics become relatively stable and the proportion of saturated hydrocarbons increases somewhat. At this time, the overall retained oil yield declines progressively, and the contents of all occurrence states generally drop to minimum values. Aliphatic chains undergo further cracking to generate small-molecule gases, and aromatic ring structures further condense to form polycyclic aromatic hydrocarbons [32]. The main peak carbon of free oil shifts toward medium-carbon-number alkanes ($nC_{20}\text{--}nC_{25}$), and the predominance of lower-carbon-number alkanes gradually disappears (Figures 8 and 9). This shift in the main peak carbon indicates that the unstable straight-chain alkanes in the saturated hydrocarbon fraction have cracked into smaller molecules and been expelled, leaving behind thermally stable medium-carbon-number naphthenes and isoalkanes, which now constitute the saturated hydrocarbon component of free oil. The aliphatic intensity of retained oil decreases, while aromatics tend to stabilize; the A-factor drops to its lowest value, and the methylene content shows a relative increase. All of these changes reflect the transformation of aliphatics through cracking or aromatization. At this stage, the proportion of free oil reaches its minimum, whereas the proportions of adsorbed–miscible oil, miscible–adsorbed oil, and adsorbed oil increase somewhat (Figure 12).

5.2. Factors Influencing the Occurrence States of Shale Oil

To elucidate the factors influencing the occurrence states of shale oil, a heatmap analysis was conducted on parameters including occurrence states, pore volume, Ro, A-factor, specific surface area, and light fractions (saturated hydrocarbons and non-hydrocarbons). The correlation coefficients are represented by colors and numerical values. The study suggests that the entire thermal evolution process can be divided into two stages for analysis, and the results are shown in Figure 13.

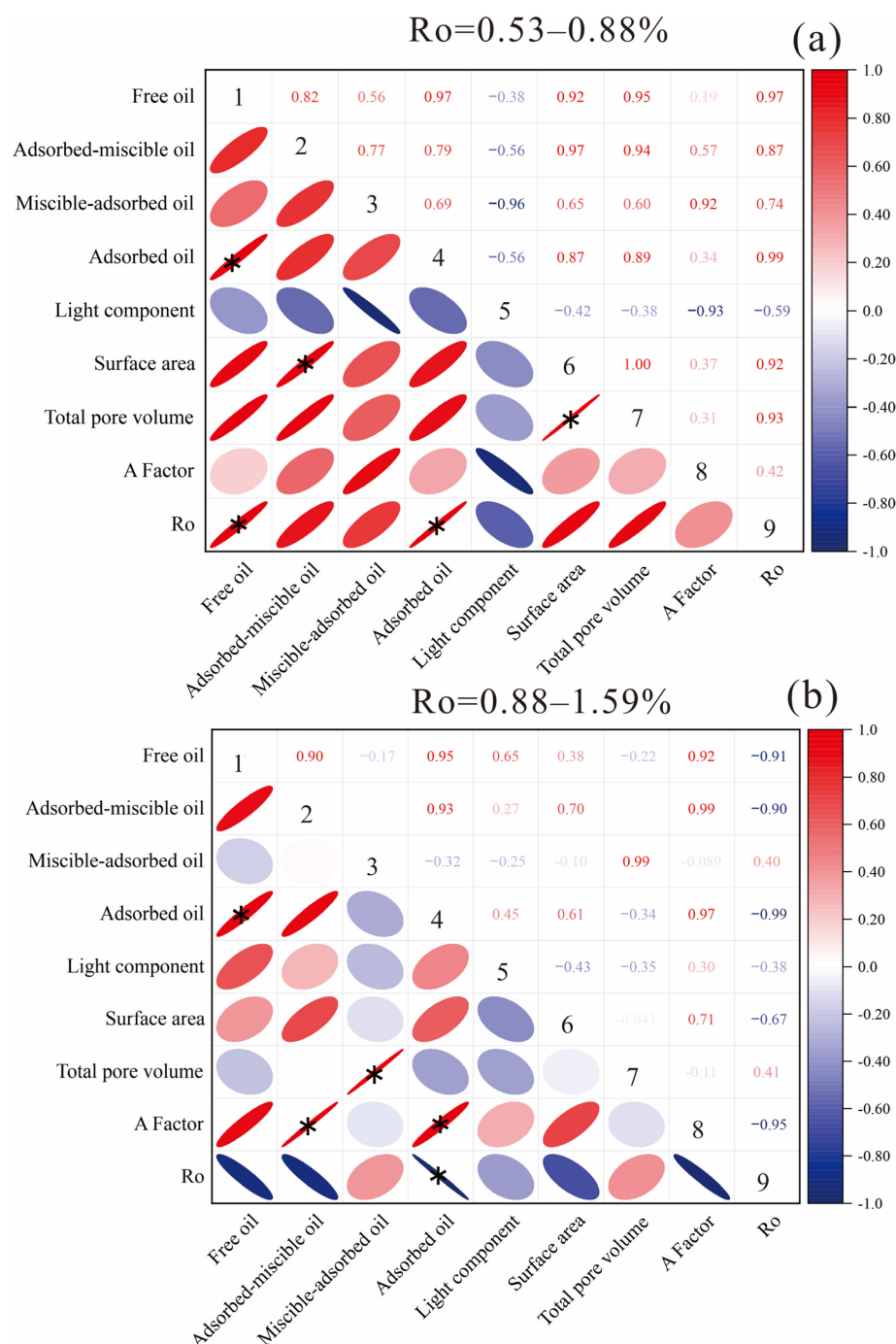


Figure 13. Correlation heatmap of the free oil, adsorbed–miscible oil, miscible–adsorbed oil, adsorbed oil, surface area, total pore volume, and light component (saturates and aromatics); (a) for stage Ro = 0.53–0.88% and (b) for stage Ro = 0.88–1.59%. * indicates *p* values less than 0.05.

When $R_o = 0.53\text{--}0.88\%$, as can be seen from the correlation coefficients, the contents of each occurrence state exhibit a direct linear relationship with both maturity (R_o) and total pore volume under the effect of thermal evolution (Figure 13a). This is because, with increasing maturity, hydrocarbon generation controls the amount of generated hydrocarbons in organic-rich shales. As kerogen cracks to generate hydrocarbons, organic matter pores begin to develop and total pore volume also increases. Therefore, hydrocarbon generation not only influences occurrence states through the quantity of hydrocarbons generated but also through pore development. Free oil and adsorbed–miscible oil show the strongest correlation trends with total pore volume, with correlation coefficients of 0.95 and 0.94, respectively. In terms of pore structure characteristics, mesopores larger than 10 nm are relatively well developed (Figure 11), which coincides with the pore size range suitable for hosting the more mobile shale oil. Free oil, adsorbed oil, and adsorbed–miscible oil show good correlations with specific surface area, with the correlation coefficients all being greater than 0.8, indicating that although specific surface area increases during evolution, it is not the primary factor determining differences in occurrence states, possibly because the increase in specific surface area provides relatively few adsorption sites. Regarding adsorption sites, some studies have shown that with increasing thermal maturity, the molecular structure of organic matter changes, especially the cleavage of aliphatic side chains and removal of oxygen-containing functional groups, which significantly alter the interaction forces between the matrix and hydrocarbons. Moreover, the absorption peak at 1700 cm^{-1} , representing oxygen-containing functional groups, is not prominent in this study, which also explains the relatively low contents of adsorbed and miscible shale oil, mainly influenced by kerogen type [33–35].

When $R_o = 0.88\text{--}1.59\%$, as indicated by the correlation coefficients, the occurrence states show pronounced correlation trends with maturity (R_o) and the A-factor during this stage, while the influences of other factors are relatively minor (Figure 13b). The correlations between most occurrence states and maturity have a negative trend, which is primarily related to the decline in yields caused by cracking of shale oil to gas. The correlations between occurrence states and light fractions are weak, suggesting that light fractions have little effect on free oil at this stage. Adsorbed oil and adsorbed–miscible oil show a strong positive correlation trend with specific surface area, which is attributed to the shrinkage of micropore volume and the consequent decrease in specific surface area, leading to a reduction in the contents of these two occurrence states. Miscible–adsorbed oil exhibits a very strong correlation with total pore volume (correlation coefficient = 0.99), indicating that this occurrence state is mainly controlled by pore volume during the secondary cracking stage of hydrocarbons. As also shown in Figure 12, the proportion of miscible–adsorbed oil increases somewhat. The A-factor behaves similarly to R_o and can to some extent reflect maturity, but more importantly, it reflects the relative abundance of aliphatic versus aromatic components. The evolution of aliphatic structures is directly controlled by the degree of thermal maturation. The rapid decline in the A-factor during this stage reflects the extensive thermal cracking and detachment of aliphatic side chains from the kerogen macromolecular structure [22,24]. After maturity exceeds $R_o = 1.42\%$, the A-factor gradually stabilizes, indicating that aliphatic components are largely consumed through cracking and expulsion. Free oil, adsorbed oil, and adsorbed–miscible oil all show strong negative correlation trends with both the A-factor and maturity, whereas miscible–adsorbed oil exhibits very weak correlations with the A-factor and maturity. This suggests that during this stage, in addition to the reduction in aliphatic structures affecting the content of miscible–adsorbed oil, total pore volume plays a dominant role in controlling its proportion, which may be related to pores smaller than 10 nm in diameter (Figure 11).

Within the current sample statistical framework, A-Factor exhibits the strongest and most stable dominant controlling effect. Although Ro and total pore volume are closely related to oil occurrence states, their effects are highly collinear with A-Factor (Figure 14). To further clarify the independent role of pore volume, a broader range of sample data is needed for validation. In terms of the evolutionary patterns observed in this study, maturity-driven hydrocarbon generation exerts a greater influence on occurrence state abundance, and the organic matter type has a larger effect on occurrence state proportions, followed by total pore volume, whereas the specific surface area and proportion of light components have relatively minor effects. Throughout this process, soluble organic matter is not only adsorbed by mineral matrix pores but also through swelling adsorption in kerogen [36].

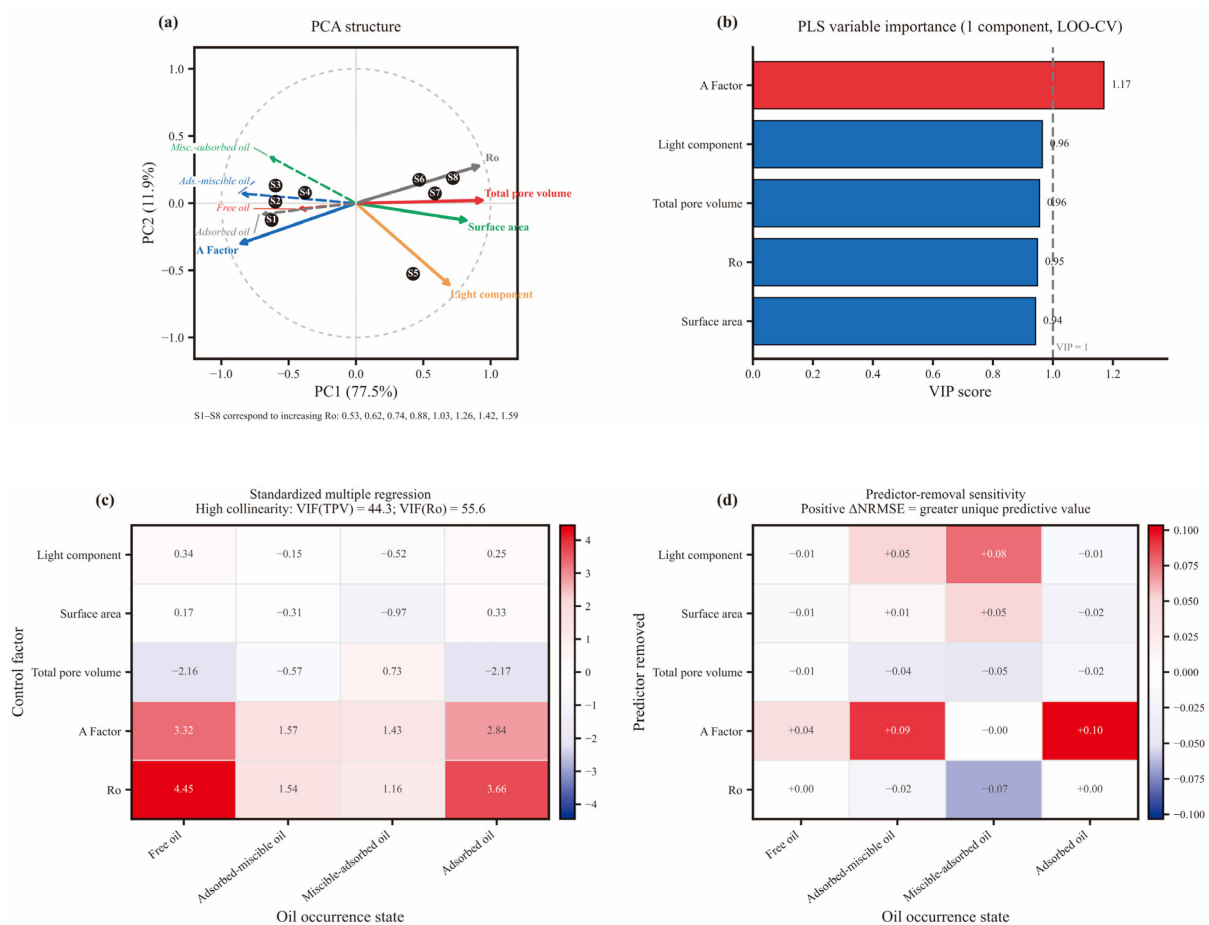


Figure 14. Principal Component Analysis (PCA) for structural analysis and Partial Least Squares (PLS) for variable importance, multicollinearity diagnosis, and predictive sensitivity analysis of the factors controlling occurrence states. (a) PCA biplot: PC1 and PC2 account for 77.5% and 11.9% of the total variance, respectively (cumulative 89.4%). Sample order (S1–S8) follows increasing maturity (Ro). (b) VIP scores from PLS: These are calculated from a partial least squares (PLS) model with one latent variable, using leave-one-out cross-validation (LOO-CV). (c) Standardized regression coefficients and collinearity diagnosis: The heatmap shows standardized coefficients of predictors on the response, controlling for other variables; red and blue indicate positive and negative effects, respectively. (d) Leave-one-variable-out sensitivity analysis: This evaluates changes in prediction error after removing each single controlling factor, based on LOO-CV.

5.3. Occurrence States Evolution Model of Organic-Rich Shale Oil

The occurrence and evolution of shale oil are dynamically controlled by the hydrocarbon generation potential of organic matter and the retention capacity of matrix pores.

Based on the yield characteristics of shale oil in different occurrence states, along with their relationships with pore structure parameters and FTIR parameters, an evolutionary model for the occurrence states of organic-rich shale oil has been established (Figure 15). Since the data are derived from the thermal simulation of a single sample, the model still has limitations.

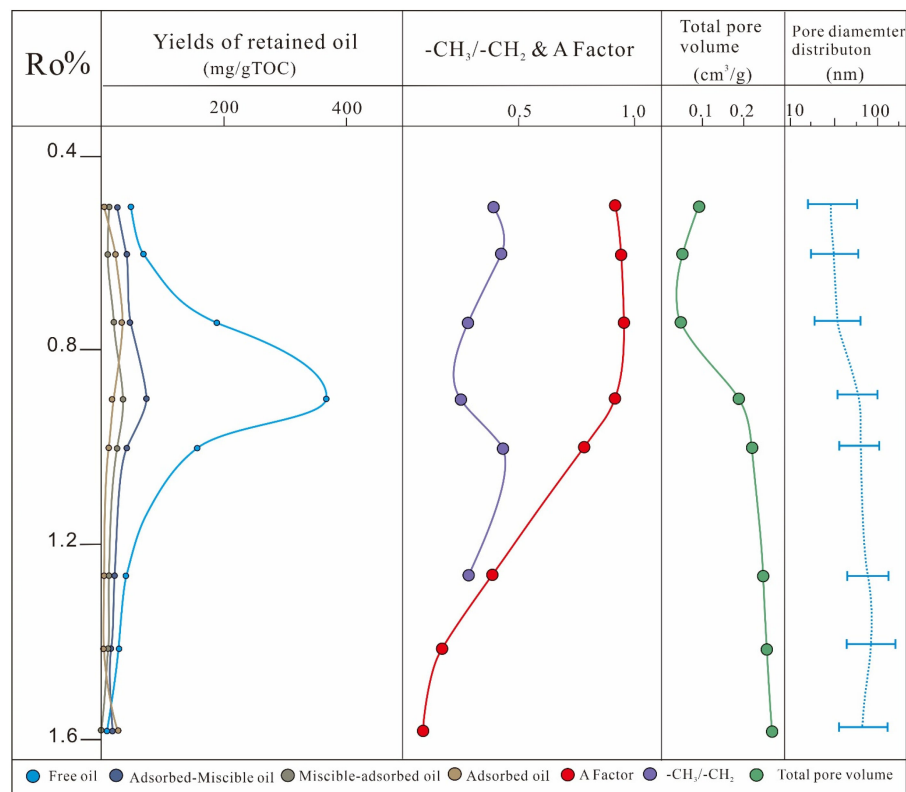


Figure 15. Evolution model of different occurrence states of rich-organic shale oil. Solid lines represent experimental observations, while dashed lines indicate conceptual extrapolations.

At the early stage ($R_o = 0.53\text{--}0.74\%$), the yields of all occurrence states remain at relatively low levels, with free oil dominating in both yield and proportion, while the yields and proportions of adsorbed–miscible oil, miscible–adsorbed oil, and adsorbed oil are comparatively low. According to previous studies, at this stage, the pore development in mudstone/shale is poor, and the pore types are mainly inorganic mineral interparticle pores and slit-shaped organic matter pores [37,38]. The pores in organic-rich shales are predominantly mesopores in the 10–50 nm range, with limited pore development and low specific surface area. The small amount of generated liquid hydrocarbons is mainly hosted in larger pores. Although the proportions of asphaltenes and non-hydrocarbons increase slightly, the occurrence state is predominantly free oil due to the large pore sizes and limited adsorption sites. During thermal evolution, the proportion of free oil begins to increase, while the proportions of adsorbed oil, miscible–adsorbed oil, and adsorbed–miscible oil decrease.

When maturity increases to $R_o = 0.74\text{--}0.88\%$, the peak oil generation stage is reached, and the yields of liquid hydrocarbons increase substantially. Concurrently, significant changes occur in the shale pore structure. Previous studies have also noted that as thermal maturity enters the oil window, thermal degradation of organic matter triggers the generation of abundant secondary organic pores [39], while the production of organic acids promotes the development of dissolution pores in feldspar and calcite, enhancing pore connectivity [40]. Meanwhile, experimental observations show that pores smaller than 10 nm

are extensively developed during this stage, and both the total pore volume and specific surface area begin to increase. At this stage, the $-\text{CH}_3/-\text{CH}_2$ ratio gradually decreases, long-chain alkanes become shorter, the proportions of saturated and aromatic hydrocarbons increase, and shale oil mobility improves. Owing to the fact that the hydrocarbon generation potential (TOC) of organic matter in this study far exceeds the adsorption-swelling capacity of the matrix, the free oil yield rises rapidly, and its proportion in the total product increases to 86.57%, reaching the maximum value. A large amount of free oil migrates from restricted micropores into newly developed organic pores, dissolution pores, and microfractures, forming the golden window for retained oil [41]. Previous studies have considered that the Ro range of 0.7–1.1% is the favorable window for free oil enrichment and flow [42]. A vitrinite reflectance of 0.75% is the maturity boundary for the transition of shale oil occurrence state and mobility, while 0.85–0.90% is the lower limit of the optimal maturity window for “high oil-bearing potential and good mobility” of shale [19]. In addition, retained oil abundance, maturity, and crude oil viscosity (including gas-oil ratio) are key factors for shale oil enrichment and high production. Within the maturity range of Ro = 0.74–1.03%, the viscosity of shale oil is typically 5–20 mPa·s, and the API gravity is generally higher than 31.1°, falling into the light to medium crude oil category with good mobility. This study suggests that the Ro = 0.74–1.03% stage, characterized by high yield and a large proportion of free oil, represents the golden window for retained oil enrichment.

During the final cracking stage (Ro = 0.88–1.59%), affected by extensive secondary cracking of liquid hydrocarbons, both the yields of free oil and adsorbed oil decrease significantly. Previous studies have indicated that as maturity enters the high-mature stage, clay minerals transform into illite, intergranular pores and shrinkage fractures in clay minerals develop, and pyrobitumen begins to form, which is rich in spongy micropores. Meanwhile, kerogen gradually condenses, and organic-matter edge fractures develop. In our experiments, macropores around 100 nm are observed to make the dominant contribution, with a peak at around 2 nm, which further confirms these observations. Previous studies have also noted that from the high-mature to the over-mature stage, small pores may decrease due to merging caused by carbonization or intense compaction [27,38], leading to a shift in pore structure toward larger pore sizes; during the over-mature stage, the pore structure of shale transforms from fine pores to larger pores. However, due to the increase in liquid hydrocarbon cracking and oil expulsion efficiency (Figure 5), the retention stage of shale oil tends to end, aliphatic components are largely consumed, shale oil mobility reaches its lowest level, the main peak carbon of saturated hydrocarbons shifts toward higher carbon numbers, and the proportion of free oil drops to its minimum.

We compared our data with the occurrence state evolution of organic-rich black shales from the Cretaceous Qingshankou Formation in the Songliao Basin, compiled by Zeng et al. [8]. Those shales are also dominated by Type I and Type II₁ kerogens, with TOC ranging from 2.31% to 13.2% and Ro from 0.58% to 1.61%. They mainly used Rock-Eval pyrolysis to evaluate free and adsorbed oil contents. Their results show that the main hydrocarbon generation window lies at Ro = 0.8–1.2%, with the maximum rate at about Ro = 1.0%; when Ro ≤ 1.2%, adsorbed oil dominates, whereas when Ro > 1.2%, free oil becomes dominant, indicating conversion from adsorbed to free oil. This differs notably from our study, where the generation window is 0.74–1.03% and the peak yields of free and adsorbed oil occur at similar maturity, both around Ro = 0.88%.

We attribute these differences primarily to the distinct principles of the two methods for evaluating occurrence states: (1) Rock-Eval pyrolysis indirectly estimates free hydrocarbon content via the S₁ peak, but the S₁ signal may partially include contributions from weakly adsorbed hydrocarbons, whereas our sequential multi-solvent extraction method, using solvents of increasing polarity, can effectively distinguish free oil, adsorbed-miscible

oil, miscible–adsorbed oil, and adsorbed oil; (2) although Zeng et al. corrected for light hydrocarbon volatilization, the programmed heating in Rock-Eval may cause desorption of some adsorbed hydrocarbons or loss of light hydrocarbons, affecting the accuracy of free oil quantification; and (3) according to the uncertainty requirements in SY/T 7661-2022 “Analytical method of pyrolysis for oil content in shale,” there is a systematic deviation between pyrolysis parameters and direct extraction methods in oil content evaluation. This also reflects the current lack of a unified methodology for shale oil occurrence state assessment.

5.4. Experimental Methods and Uncertainty Analysis

Multi-solvent sequential extraction is the core method for distinguishing different occurrence states, based on differences in storage space and molecular polarity among hydrocarbon fractions in various occurrence states. However, extraction efficiency is jointly controlled by solvent properties, rock characteristics, and extraction time. Studies have shown that more than 80% of soluble fluids can be removed within 7 days [43]. In an open environment, pressure release and temperature reduction cause significant loss of light hydrocarbons; research indicates that processes such as grinding and Rock-Eval waiting can result in cumulative loss of up to approximately 60% of in situ hydrocarbons [44]. Meanwhile, microcrack closure and surface tension may physically trap part of the free oil inside the particles, leading to systematic underestimation of measured values. In addition, errors in stepwise extraction mainly arise from differences in solvent polarity and light hydrocarbon loss during crushing [45]. Low-polarity solvents may carry off some weakly adsorbed hydrocarbons during free oil extraction, and there is a continuous transition in molecular composition among different occurrence states rather than a sharp division; therefore, the boundary between “adsorbed–miscible oil” and “miscible–adsorbed oil” is inherently ambiguous.

In thermal simulation experiments under high-temperature and high-pressure conditions, samples are prone to fragmentation. Although the semi-open system is the closest to geological reality, it still cannot precisely replicate the actual expulsion volume and expulsion processes in real geological history. Moreover, sample fragmentation caused by high temperature and pressure tends to increase expulsion efficiency and enlarge pore spaces, thereby affecting the proportion of free oil.

The theoretical foundation of thermal simulation experiments is the “time–temperature compensation principle,” according to which organic matter thermal evolution is governed by both temperature and time, and the two can compensate for each other within certain limits. However, extrapolating kinetic parameters derived at high temperatures (e.g., activation energies) to low-temperature geological systems via the Arrhenius equation inherently suffers from theoretical flaws, as reaction pathways may differ across temperature ranges. Furthermore, the Easy%Ro model tends to overestimate vitrinite reflectance at high maturity compared to measured values [29]. Therefore, in addition to empirical models, directly measured Ro values are more representative of actual maturity.

5.5. Occurrence Characteristics of Other Shale Systems

Significant differences exist between marine shales (e.g., the Longmaxi Formation in the Sichuan Basin) and continental shales in terms of pore structure and occurrence mechanisms. In pore structure, marine shales have smaller pore sizes and higher fractal dimensions than continental shales, indicating more complex pore structures [46]. The marine shale of the Longmaxi Formation contains densely interconnected honeycomb-like pores within individual organic matter particles, with micropores being the most developed, providing ample specific surface area for adsorbed hydrocarbon occurrence. In contrast, continental shales (e.g., the lower sub-member of the Es₃ in the Zhanhua

Sag) do not develop such densely distributed honeycomb-like pores within organic matter particles; instead, macropores are more developed, providing storage space for free hydrocarbon occurrence [47]. Marine shales are dominated by Type II kerogen, with organic pores controlled by maturity and maceral composition, and their enrichment mechanism is characterized by “source–reservoir integration, in situ accumulation, and late-stage modification.” In contrast, continental shales exhibit strong heterogeneity and complex mineral compositions, with occurrence states jointly governed by pore volume and mineral surfaces.

Typical North American marine shale systems have been extensively studied in terms of retained hydrocarbon characteristics. Research on the Barnett Shale has revealed compositional fractionation during in-reservoir oil migration, retention, and expulsion. Lithological heterogeneity controls the composition and quantity of retained fluids, and adsorption of oil onto solid organic matter is important across all intervals. Mass balance calculations indicate that short-distance migration causes compositional fractionation of generated oil, with polar compounds preferentially retained in organic-rich and clay-rich intervals, with the retention order being: polar compounds > aromatics > saturated hydrocarbons [48]. The overpressure generated by hydrocarbon generation in the Bakken Formation is greater than that in the Eagle Ford Formation, providing a larger expulsion driving force, resulting in less retained oil and gas in the Bakken, whereas most of the oil and gas in the Eagle Ford remain retained in situ [49]. The high maturity and extensively developed organic pores in North American marine shales determine their predominantly free-state occurrence, while mineral composition (biogenic framework, clay content) and overpressure development are common factors controlling retention efficiency and compositional fractionation.

In the Qingshankou Formation of the Songliao Basin, shale oil occurrence states are defined as free oil, free-adsorbed oil, and adsorbed oil extracted from different grain sizes under cold extraction and Soxhlet extraction conditions. Free oil is mainly composed of light components, while adsorbed oil contains more heavy components; larger pores are dominated by free oil, whereas adsorbed oil is mostly distributed in smaller pores. The compositional variations between free and adsorbed oils reveal compositional fractionation during micro-migration of petroleum expulsion—oil after migration has higher saturated hydrocarbon + aromatic hydrocarbon contents, smaller molecular size, and lower Pr/n-C₁₇ and Ph/n-C₁₈ ratios, indicating greater mobility potential [50]. In terms of thermal evolution, the main storage space for shale oil shifts from kerogen to rock and organic-hosted pore-fractures at low- to medium-evolution stages, and from adsorbed to free state at medium- to high-evolution stages. In the lacustrine shale of the Paleogene Shahejie Formation in the Jiyang Depression, Bohai Bay Basin, different lamina assemblages exert a decisive control on occurrence states: in the “organic-rich + argillaceous” binary lamina assemblage mudstone, shale oil occurs predominantly as free oil in interlayer fractures with the best mobility; in the “organic-rich + argillaceous” binary lamina assemblage mudstone, free oil and adsorbed oil coexist with relatively poorer mobility; whereas in the “organic-rich + felsic” binary lamina assemblage mudstone, shale oil mainly occurs as adsorbed oil with the poorest mobility [51].

In the future, the higher-order nonlocal generalized particle dynamics (NGPD) method can be employed to extend the occurrence-state evolution patterns revealed in this study into a multiphase and multi-field coupled numerical simulation framework [52]. The recently developed fully coupled four-phase dynamic model for shale reservoirs based on higher-order NGPD provides a new approach for investigating multiphase flow and mass transport in shale. Introducing NGPD into shale oil occurrence-state modeling is expected to achieve a leap from “static experimental characterization” to “dynamic multi-field

coupled prediction,” thereby providing theoretical support for quantitatively forecasting the spatiotemporal evolution of retained hydrocarbon occurrence states.

6. Conclusions

Based on semi-open system thermal simulation experiments, GC–MS, low-temperature N_2 adsorption, FTIR, and sequential multi-solvent extraction were conducted. The evolution patterns of retained oil occurrence states in organic-rich shales remain unclear, which is a key research focus in the field of lacustrine shale oil. Building on previous studies that have characterized the static occurrence features, pore evolution, and hydrocarbon generation evolution of shale oil well, this study determined the occurrence-state evolution characteristics of organic-rich shales with maturities ranging from 0.53% to 1.59% Ro. On this basis, combined with group-type composition, pore structure, and FTIR characteristics, an evolutionary model for the occurrence states of organic-rich shale oil was established.

- (1) According to the yield of each occurrence state, the evolution process is divided into three stages. In the Ro = 0.53–0.74% stage, the yields of all occurrence states increase slowly, and pore development is poor. In the Ro = 0.74–1.03% stage, shale oil yield shows explosive growth with extensive pore development, and the proportion of free oil increases to 76.84–86.57%. In the Ro = 1.03–1.59% stage, shale oil cracks to gas, yields gradually decrease, and the free oil proportion drops to 25.83%. It is suggested that the Ro = 0.74–1.03% stage represents the golden window for free oil enrichment and is the optimal maturity range for exploration and development.
- (2) Based on the parameter analysis of factors influencing occurrence states, the thermal evolution process of organic-rich shale is divided into two stages. At Ro = 0.53–0.88%, each occurrence state shows a certain positive correlation trend with maturity and total pore volume. The proportion of free oil steadily increases and dominates, which is mainly attributed to the fewer oxygen-containing functional groups and the pore size range of 20–100 nm. At Ro = 0.88–1.59%, free oil, adsorbed oil, and adsorbed–miscible oil exhibit a negative correlation trend with maturity and no significant correlation with total pore volume. Miscible–adsorbed oil shows a weak positive correlation with maturity and a certain positive correlation trend with total pore volume.

In addition to the influences of maturity, composition, and pore structure characteristics, the content and type of minerals are also crucial to the evolution of occurrence states. However, this study lacks an investigation into the role of minerals in occurrence state evolution. In future research, we will systematically conduct a quantitative characterization of the effects of different mineral types and contents on the evolution of occurrence states.

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