

The Influence of Extractable Organic Matter on Pore Development in the Late Triassic Chang 7 Lacustrine Shales, Yanchang Formation, Ordos Basin, China

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Abstract: To investigate the influence of extractable organic matter (EOM) on pore evolution of lacustrine shales, Soxhlet extraction, using dichloromethane, was performed on a series of Chang 7 shale samples (Ordos Basin, China) with vitrinite reflectance of 0.64% to 1.34%. Low-pressure gas adsorption experiments were conducted on the samples before and after extraction. The pore structure parameters were calculated from the gas adsorption data. The results show complex changes to the pore volumes and surface areas after extraction. The pore development of both the initial and extracted samples is strongly controlled by total organic carbon (TOC) content. Micropores developed mainly in organic matter (OM), while mesopores and macropores predominantly developed in fractions other than OM. The influence of EOM on micropores is stronger than on mesopores and macropores. Organic solvents with a higher boiling point should be used to explore the effect of EOM on pore structure in the future.

Key words: lacustrine shale, pore development, extraction, shale gas, Chang 7, Ordos Basin

1 Introduction

Recently, shales have been extensively researched as reservoir rocks for oil and gas worldwide, due to the successful production of shale oil and shale gas in North America and China (Jarvie et al., 2007; Guo and Zhang, 2014; Zhao et al., 2016). The pore properties of shales have an important influence on the capacity for storing oil and gas (Ross and Bustin, 2009; Ma et al., 2015; Xiong et al., 2015; Wang et al., 2015a, b; Han et al., 2016a). Pores in shales can be classified into interparticle pores, intraparticle pores and organic matter (OM) pores (Loucks et al., 2012). The abundance of these three types of pores

in shales is mainly controlled by the mineralogical composition and organic matter content (Ross and Bustin, 2009; Ma et al., 2015; Xiong et al., 2015; Wang et al., 2015a, b; Han et al., 2016a). In addition, the pore volume, surface area, and size distribution vary with maturity.

Previous studies have considered the pore evolution of shales. Mastalerz et al. (2013) found the pore volume of New Albany shale samples increased initially and then increased with increasing maturity (0.35%–1.41% R_o), which was attributed to the generation and expulsion of liquid hydrocarbons. Chen and Xiao (2014) presented the micropore and mesopore characteristics of a series of artificial shale samples with equivalent vitrinite reflectance values ranging from 0.69% to 4.19%. The

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formation and evolution of nanopores in shales were divided into formation stage ($0.60\%–2.0\%R_o$), development stage ($2.00\%–3.5\%R_o$), and conversion or destruction stage ($>3.5\%R_o$) by them. Hu et al. (2015) observed that the porosity of shales increased with maturity from a series of artificial shale samples, ranging from immature to the oil-cracking stage. Curtis et al. (2012) concluded that the secondary organic porosity was not a linear function of thermal maturity by observing eight samples of Woodford shale with mean random vitrinite reflectance values ranging from 0.51% to 6.36%. Romero-Sarmiento et al. (2014) showed that the nanoporosity increased with increasing maturity. Pommer and Milliken (2015) concluded that primary porosity decreased and the secondary organic matter porosity increased during diagenesis based on the shale samples with maturities ranging from 0.5% to $1.3\%R_o$ from the Eagle Ford Formation in the Maverick Basin. Ko et al. (2016) demonstrated that original interparticle and intraparticle pores are functions of depositional and early diagenetic processes before petroleum generation and migration; pore evolution was closely related to organic matter conversion when organic matter became mature. Guo et al. (2017) compared the pore evolution of two series of artificial shale samples from a closed system and a semi-closed system, using Chang 7 shale samples as starting materials, showing that there is no straightforward relationship between organic matter decomposition and pore development. The works above indicated that pore evolution is obviously different between shales from various basins. Moreover, most of these works considered marine shales, meaning that the pore evolution of lacustrine shales remains poorly understood.

The pore volumes of New Albany shales increase at first and then decrease with increasing maturity (Mastalerz et al., 2013). This evolution of pore volume was explained by the generation of oil-filling pores, followed by the release of pore space by oil cracking. The pore volumes of shales show a marked increase after extraction (Valenza II et al., 2013; Guo et al., 2014; Mohnhoff et al., 2016), which indicates that the retained oil occupies a large volume of pore space in shales, especially shales with a maturity within the oil window. Li et al. (2016) found that both soluble and insoluble organic matter occupied plenty of pore space in the shale from the Yanchang Formation in the Ordos Basin. The influence of soluble organic matter on pore evolution in shales has been evaluated by Wei et al. (2014). Their results demonstrated that the trends of pore volume and surface area of the extracted samples were similar to the original ones. Although it has been shown that oil generation and cracking have an important influence on the pore evolution of shales, the lacustrine

shale samples at various maturity levels extracted using organic solvents has not been well documented.

The shales of the Chang 7 member of the Triassic Yanchang Formation of the Ordos Basin in China have good potential for oil and gas (Lei et al., 2015). The pore characteristics of the Chang 7 shales have been studied previously. These studies mainly focused on fractal analysis (Liu et al., 2015; Jiang et al., 2016; Han et al., 2018), pore evolution (Sun et al., 2015; Chen et al., 2016), and the effects of retained oil on pores (Guo et al., 2014; Li et al., 2016; Xiong et al., 2016). The pore network in the shales from the Yanchang Formation is dominated by intraparticle pores and a lesser abundance of organic matter pores, as well as organic matter pores mainly developed in solid bitumen (Loucks et al., 2017). Compared with the marine Eagle Ford shales, the Chang 7 shales lack early cementation during compaction (Ko et al., 2017). The pore development of shales from the Yanchang Formation was jointly controlled by compaction, the petroleum expulsion process, and the organic matter type (Guo et al., 2018). However, previous studies of pore characteristics in the Chang 7 shales at various maturity levels were performed using artificial samples (e. g., Sun et al., 2015; Chen et al., 2016; Guo et al., 2017). Pores in natural samples with various maturities may show different results to those obtained previously.

In the present contribution, a maturity series of lacustrine shale samples was chosen from the Chang 7 member of the Triassic Yanchang Formation in the Ordos Basin. The selected samples were extracted using dichloromethane. Low-pressure gas (CO_2 and N_2) adsorption experiments were performed on the samples before and after extraction to obtain their pore structure parameters. The pore characteristics of the initial and extracted shale samples were analyzed. The results improve our understanding of pore structure in lacustrine shales and provide insights into oil storage in shale.

2 Geological Setting and Sampling

The Ordos Basin in central China (Fig. 1) covers an area of $32 \times 10^4 \text{ km}^2$ and consists of six structural units: the Yimeng uplift in the north, the Weibei uplift in the south, the Tianhuan depression in the west, a thrust belt on its western edge, the Jinxi fold belt in the east, and the Yishan slope in the center (Duan et al., 2008) (Fig. 1). The Yishan slope is the largest structural unit in the basin, and strata in the unit dip at $<1^\circ$ towards the west. The basement of the basin is crystalline rock of the Archean Eonothem and Palaeoproterozoic, which has experienced five tectonic stages: Meso-neoproterozoic aulacogen, early Paleozoic shallow marine platform, late Paleozoic

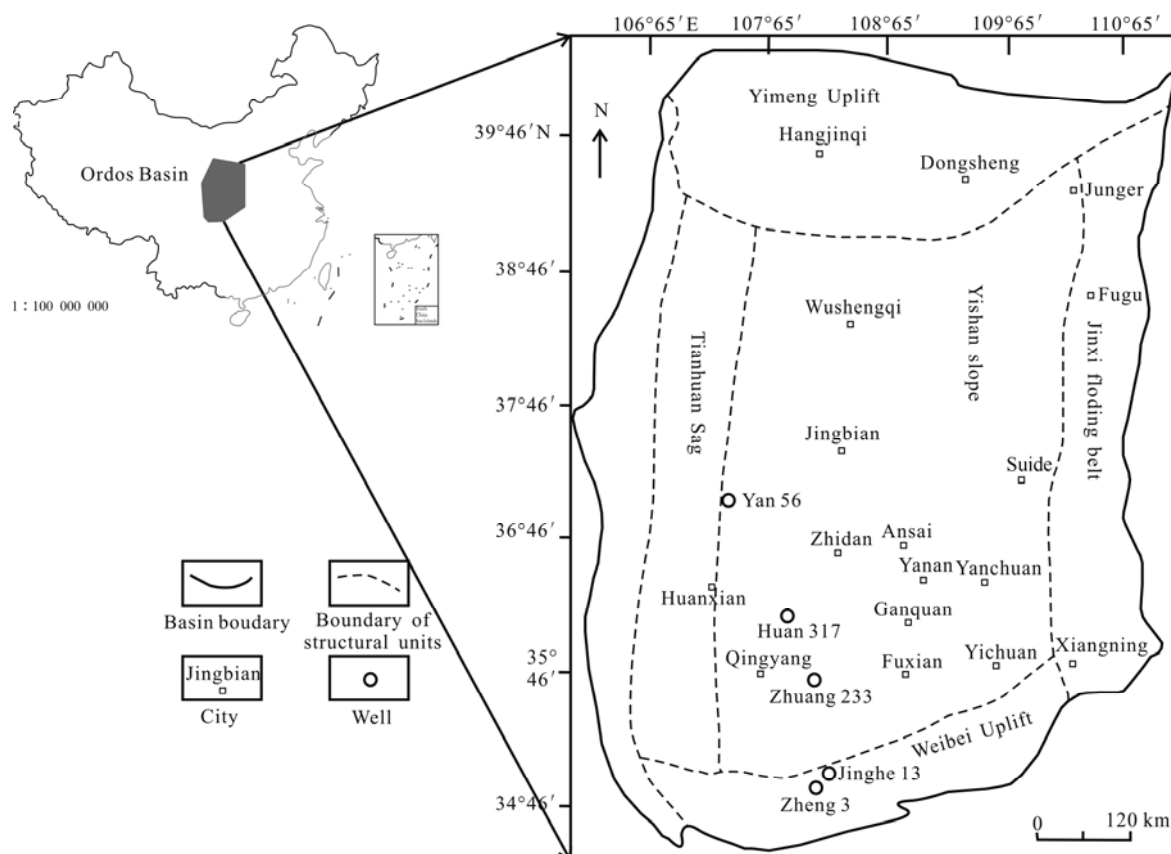


Fig. 1. Locations of sampling wells and regional tectonic profile across the Ordos Basin (China basemap after China National Bureau of Surveying and Mapping Geographical Information).

offshore plain, Mesozoic inland depression, and Cenozoic fault depression (Yang et al., 2005). The main tectonic framework of the Ordos Basin largely developed during the Mesozoic. Widespread lacustrine shales formed during the Late Triassic. Lacustrine shales of the Triassic Yanchang Formation are the main source rocks for conventional oil resources in the basin (Duan et al., 2008). This basin has undergone five reworking episodes since the Late Cretaceous (Zhao et al., 2011). The current tectonic setting developed after Cenozoic subsidence.

The Yanchang Formation consists of Upper Triassic strata and is divided into 10 members, Chang 1–10 from top to bottom (Fig. 2), which consists of mudstones, shales, and sandstones. Chang 7 is composed predominantly of shales (Zhang et al., 2009) and is an important exploration target for shale gas (Lei et al., 2015). In this study, 8 samples from the Chang 7 member were collected from the cores of wells Zheng 3, Zhuang 233, Jinghe 13, Yan 56 and Huan 317 (Fig. 1).

3 Experiments

3.1 Geochemical measurements

After surface cleaning, core samples were crushed to 100 mesh (<150 μm), and the geochemical parameters of

the powdered samples were measured using a Rock-Eval II instrument in accordance with the method of Espitalie et al. (1977). The parameters of S_1 , S_2 , hydrogen index (HI), and T_{max} can be obtained from Rock-Eval pyrolysis. The studied samples were subjected to programmed heating at an inert atmosphere to determine the amount of volatile gas (S_1) and the amount of nonvolatile hydrocarbons (S_2) released during thermal cracking of the kerogen in the rock. T_{max} value is determined from the temperature at the peak of S_2 . A CS-230 elemental analyzer was used to determine total organic carbon (TOC) content following the standard procedure (SY/T 5116-1997). HI is calculated using S_2 and TOC ($\text{HI} = 100 \times S_2 / \text{TOC}$). A D/MAX 2500 X-ray diffractometer was used to measure their mineral compositions. The vitrinite reflectance of the studied samples was measured using an MPV-III microphotometer (Taylor et al., 1998).

3.2 Soxhlet extraction

To obtain comparable results with the previous works (e. g., Valenza II et al., 2013; Guo et al., 2014), Soxhlet extraction was performed on the powdered samples (60 mesh) using a 25:2 vol/vol mixture of dichloromethane and methanol for 72 hours. Rock-Eval pyrolysis and TOC content measurements were performed on the extracted

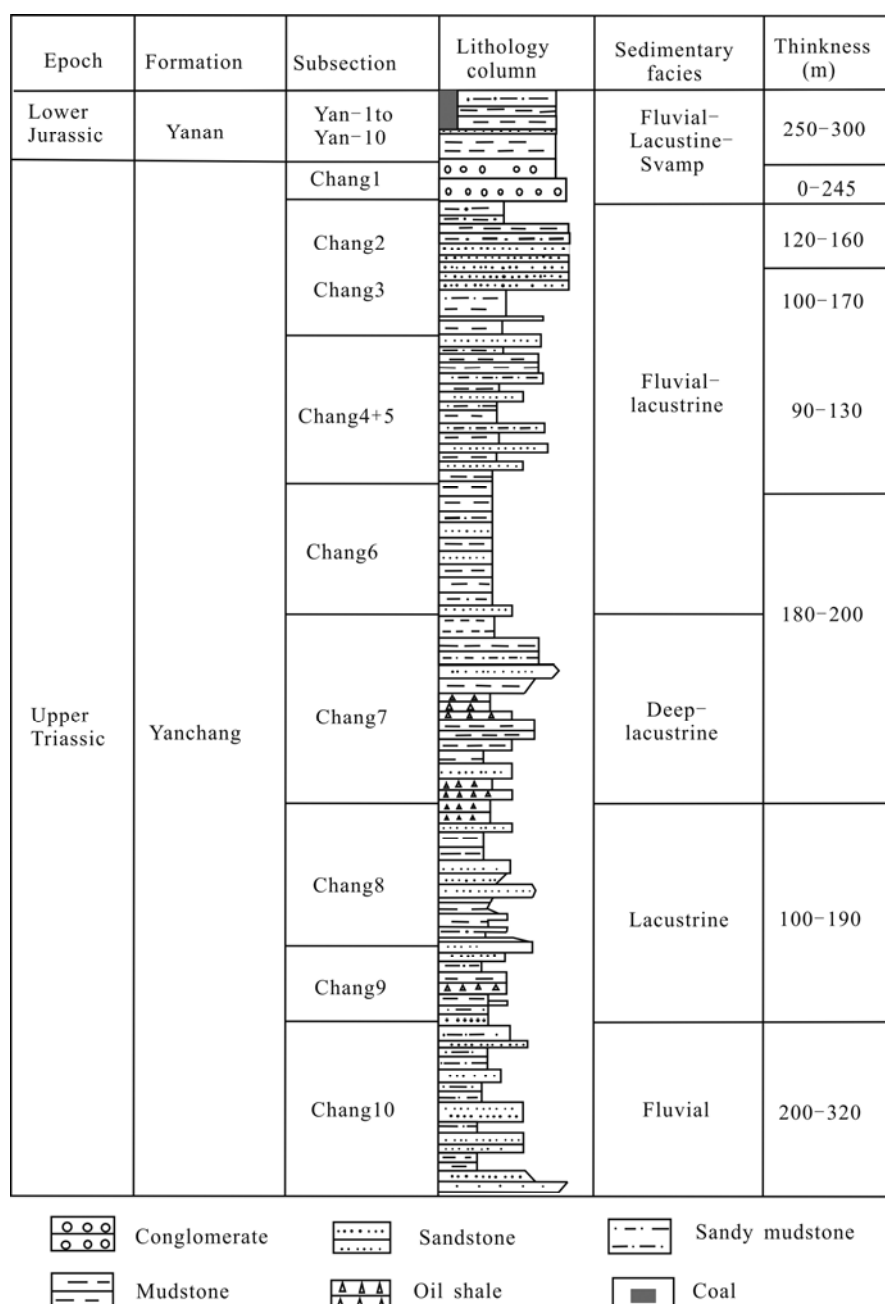


Fig. 2. Upper Triassic and Lower Jurassic stratigraphy and depositional environment of the Yanchang Formation (modified from Guo et al., 2014).

shale samples. The extracts from each sample were separated into saturated hydrocarbons, aromatic hydrocarbons, polar compounds and asphalt, using open silica gel column chromatography (Yang et al., 2015).

3.3 Low-pressure gas adsorption experiments

Although Han et al. (2016b) suggested a particle size of 130 mesh for low-pressure gas adsorption experiments of shales, 60 mesh is most widely used. Therefore, the samples were crushed to 60 mesh to ensure the results could be compared with those of previous studies. Before

and after extraction the crushed samples were dried in an oven overnight at 110 °C and degassed under a high vacuum (<10 mmHg) for 12 hours at 110 °C (Tian et al., 2013).

A Micromeritics® ASAP 2020 instrument was used for the low-pressure gas (CO₂ and N₂) adsorption experiments. In the process of the experiments, 1–2 g of each of the samples was exposed to CO₂ and N₂ at temperatures of 0°C and –196.15°C, respectively. CO₂ and N₂ adsorption volumes were measured over the relative pressure (P/P₀) ranges of 0.0005–0.0300 and 0.050

−0.995, respectively, where P_0 represents the condensation pressure of CO_2 or N_2 under laboratory conditions, and P is the actual gas pressure.

The density functional theory (DFT) method can provide an accurate description of the thermodynamic properties of the gas in the pores (Neimark et al., 2009). Although the results of the DFT method have been considered unreliable (Bertier et al., 2016), the parameters for the pore structure of the studied samples were calculated using this method (Do and Do, 2003; Zhang and Yang, 2013). In the calculation of N_2 adsorption, the data from the adsorption branches of the isotherms were used.

4 Results

4.1 Geochemical and mineral characteristics

The geochemical parameters of the initial samples are listed in Table 1. The TOC content varied from 1.46 to 25.1 wt% and averaged 9.27 wt%. The vitrinite reflectance (R_0) values of the studied samples are between 0.64% and 1.34%. The organic matter types in the initial samples were determined using the HI vs. T_{max} diagram in Figure 3 (Espitalie et al., 1985), which suggests Type II organic matter predominates. The geochemical parameters of the extracted samples are listed in Table 2. Compared with the initial samples, the TOC content, S_1 and S_2 have all decreased due to extraction. The amount of free hydrocarbons normalized to TOC content (S_1/TOC) showed a maximum value at $\sim 0.7\%R_0$, which may indicate the peak of the oil window.

The mineral compositions of the initial samples are listed in Table 3. The dominant fractions are clays (28.67–60.65 wt%), quartz (22.13–43.20 wt%) and feldspar (6.91

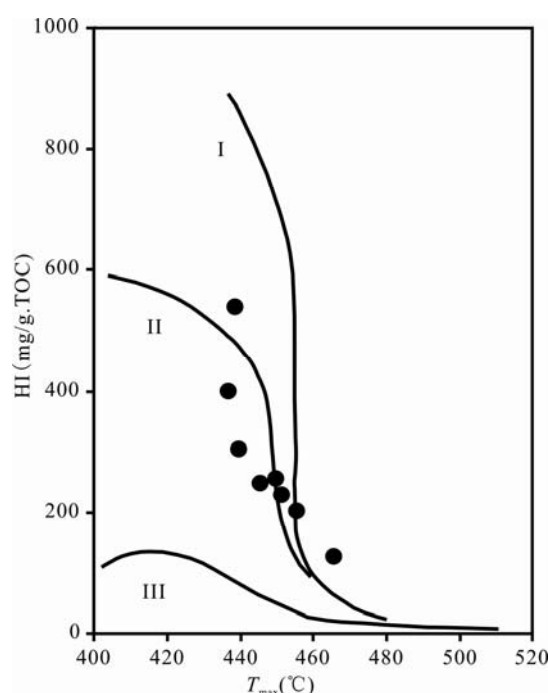


Fig. 3. HI vs. T_{max} diagram for the studied samples (based on Espitalie et al., 1985).

–15.30 wt%). Mixed-layer illite and smectite account for 53–77 wt% of the clays, with an average of 63.38 wt%.

4.2 Composition of the extracts

The yields and compositions of extractable organic matter of the studied samples are listed in Table 4. The amounts of extractable organic matter (EOM) of the studied samples range from 0.07 to 0.94 wt% with an average of 0.51 wt %. The varying ranges of saturated hydrocarbons, aromatic hydrocarbons, polar compounds, and asphalt are 20.56–58.56 wt%, 13.17–29.91 wt%, 8.99

Table 1 Geochemical data of the initial samples

Sample	Well	Depth (m)	TOC (wt %)	T_{max} (°C)	S_1 (mg/g.rock)	S_2 (mg/g.rock)	S_1+S_2 (mg/g.rock)	HI (mg/g.TOC)	R_0 (%)
1	Yan 56	2963.1	6.09	446	2.98	14.91	17.89	245	0.64
2	Yan 56	2978.5	6.29	450	3.02	15.88	18.90	252	0.69
3	Yan 56	2996.5	6.25	452	3.11	14.32	17.43	229	0.71
4	Jinghe 13	1357.23	1.46	440	0.29	5.68	5.97	302	0.72
5	Zheng 3	866.74	3.82	437	0.62	15.16	15.78	397	0.83
6	Zhuang 233	1798.7	25.10	439	10.43	135.13	145.56	538	0.84
7	Huan 317	2468.3	18.10	456	4.81	36.07	40.88	199	1.28
8	Huan 317	2474.3	7.95	466	2.78	9.89	12.67	124	1.34

Table 2 Geochemical data of the extracted samples

Sample	Well	Depth (m)	TOC (wt %)	T_{max} (°C)	S_1 (mg/g.rock)	S_2 (mg/g.rock)	S_1+S_2 (mg/g.rock)	HI (mg/g.TOC)
1	Yan 56	2963.1	4.22	444	0.55	10.92	11.47	259
2	Yan 56	2978.5	4.50	440	0.60	9.68	10.28	215
3	Yan 56	2996.5	4.62	452	1.25	11.29	12.54	245
4	Jinghe 13	1357.23	1.03	436	0.14	3.09	3.23	300
5	Zheng 3	866.74	2.67	432	0.36	10.61	10.97	397
6	Zhuang 233	1798.7	16.78	438	1.14	71.93	73.07	298
7	Huan 317	2468.3	14.52	452	1.32	25.29	26.61	174
8	Huan 317	2474.3	7.08	456	0.84	10.54	11.38	149

Table 3 Mineralogical composition of the studied samples

Sample	Relative percent (wt%)								Clay relative percent (wt%)			
	quartz	feldspar	calcite	dolomite	pyrite	siderite	aragonite	clays	I/S ^a	illite	kaolinite	chlorite
1	24.00	15.30			2.10	1.30	13.80	43.50	53	18	13	16
2	29.30	10.80				4.00		55.90	57	17	12	14
3	31.50	12.50				6.60		49.40	64	17	11	8
4	43.20	11.40	0.8	4.7				39.9	64	22	2	12
5	26.0	8.90			9.5			55.6	59	20	8	13
6	23.44	6.91				40.98		28.67	70	22	3	5
7	22.13	8.20	2.27			19.04		48.36	69	25	3	3
8	24.82	9.29				5.24		60.65	71	21	4	4

^a I/S: mixed-layer minerals of illite and smectite.

Table 4 Yield and composition of extractable organic matter in the studied samples

Sample	R_o (%)	EOM ^a (wt%)	Saturated ^b (wt%)	Aromatic (wt%)	Polar compounds (wt%)	Asphalt (wt%)
1	0.64	0.64	49.35	19.11	11.13	18.00
2	0.69	0.69	45.85	20.96	24.89	7.42
3	0.71	0.59	48.47	15.64	24.54	7.67
4	0.72	0.07	38.54	21.50	21.30	15.21
5	0.83	0.23	30.59	25.24	18.52	16.32
6	0.84	0.94	20.56	29.91	28.04	21.03
7	1.28	0.37	28.97	21.43	24.60	17.06
8	1.34	0.58	58.56	13.17	8.99	13.17

^a EOM: extractable organic matter. ^b The relative contents of saturated, aromatic, polar compounds and asphalt are reported relative to EOM.

–28.04 wt% and 7.42–21.03 wt%, respectively. With the increase of maturity, the heavy components (aromatic hydrocarbons, polar compounds and asphalt) increase ($0.64\% R_o$ – $0.84\% R_o$) firstly and then decrease, while saturated hydrocarbons show an opposite trend (Fig. 5).

4.3 Isotherms

4.3.1 Low-pressure CO₂ adsorption

Figure 6 shows the low-pressure CO₂ adsorption (LPGA-CO₂) isotherms of the studied samples. All the isotherms are Type I, which indicates the shale samples are microporous solids. For all the samples, the volume of sorbed CO₂ for the extracted sample is greater than that for the initial sample.

4.3.2 Low-pressure N₂ adsorption

The low-pressure N₂ adsorption (LPGA-N₂) isotherms

of the studied samples (Fig. 7) are classified as Type II (Brunauer et al., 1940). In most cases, the sorbed N₂ volumes for the extracted samples are higher than those for the corresponding initial samples (Fig. 7a–d, g–h). For samples 5 and 6 there is no significant change in sorbed N₂ volumes between the extracted and initial samples (Fig. 7e–f). For samples 3, 7, and 8, the hysteresis loops of the extracted samples are not closed (Fig. 7c, g–h), which may be related to swelling or the adsorption of nitrogen in micropores (Gregg and Sing, 1982).

4.4 Pore volume and surface area

The pore volumes and surface areas obtained from the LPGA-CO₂ and LPGA-N₂ experiments are listed in Tables 5 and 6, respectively. The pore classification of Rouquerol et al. (1994) is used. The diameter ranges of micropore, mesopore, and macropore are 0–2 nm, 2–50 nm and >50

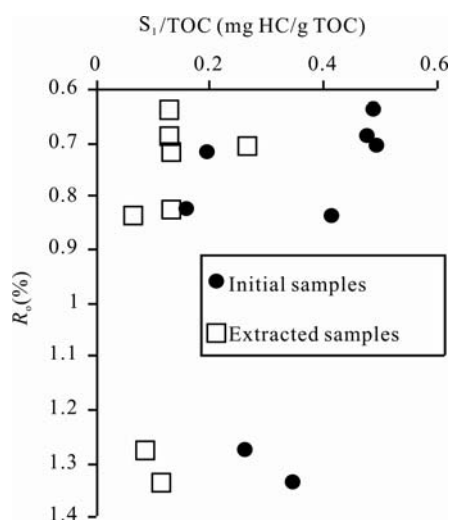


Fig. 4. S_1 /TOC vs. R_o diagram for the studied samples.

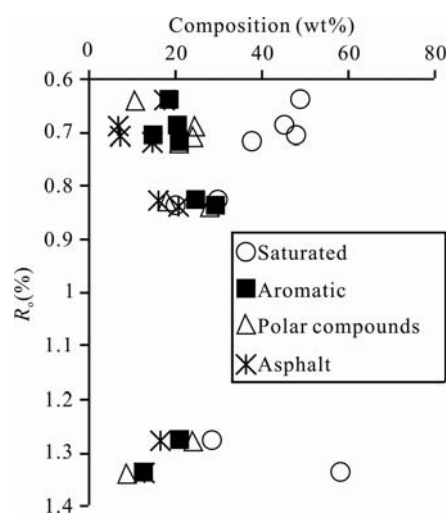


Fig. 5. Composition of extractable organic matter vs. R_o for the studied samples.

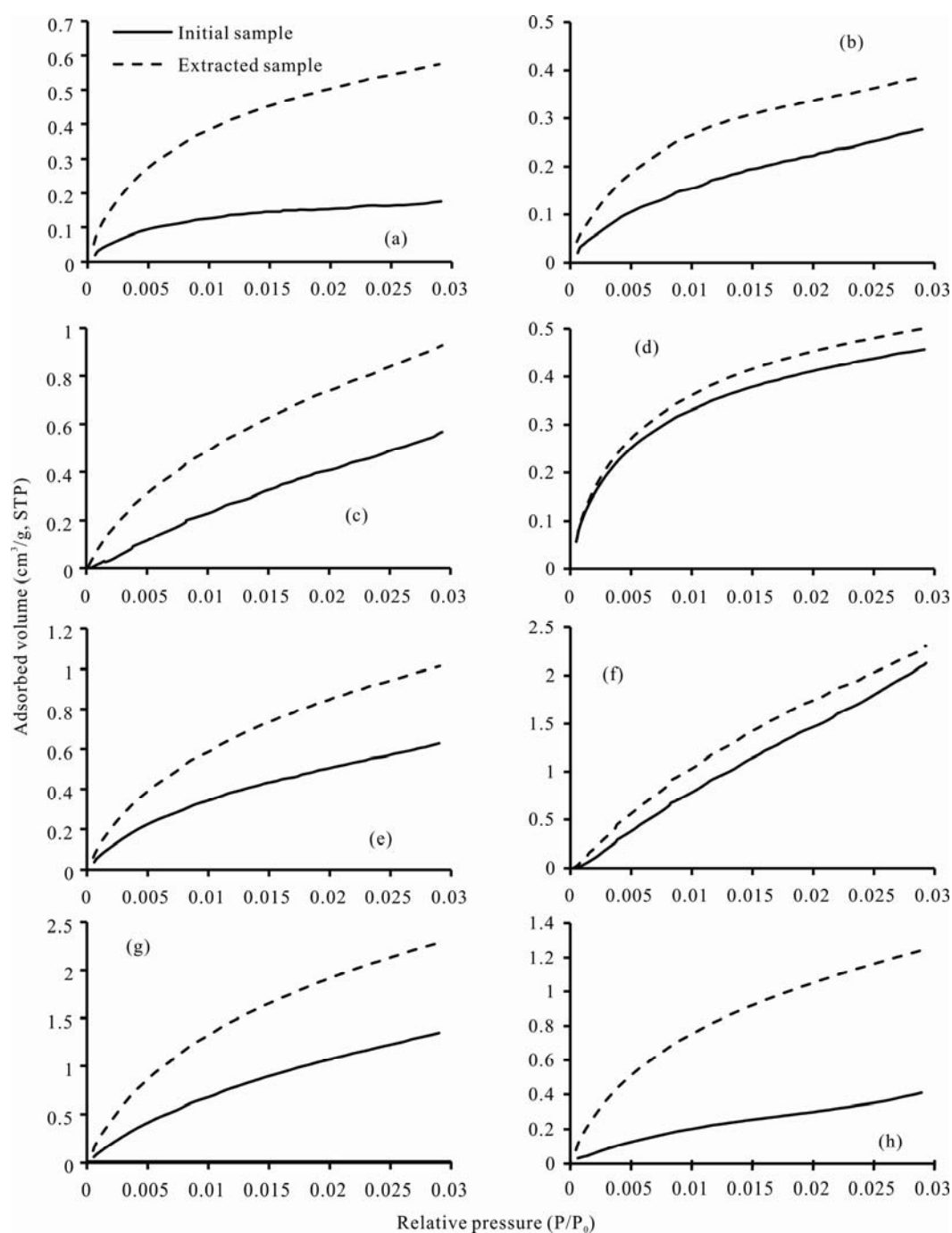
Fig. 6. Low-pressure CO₂ adsorption isotherms for the studied samples.

Table 5 Pore volume data of the studied samples

Sample	Initial samples (cm ³ /g)				Extracted samples (cm ³ /g)			
	micropore	mesopore	macropore	total	micropore	mesopore	macropore	total
1	0.0004	0.0111	0.0031	0.0146	0.0004	0.0115	0.0029	0.0149
2	0.0010	0.0109	0.0034	0.0152	0.0010	0.0103	0.0026	0.0139
3	0.0021	0.0077	0.0019	0.0117	0.0033	0.0106	0.0024	0.0163
4	0.0016	0.0162	0.0034	0.0213	0.0022	0.0170	0.0037	0.0228
5	0.0023	0.0128	0.0040	0.0191	0.0023	0.0121	0.0046	0.0190
6	0.0079	0.0059	0.0024	0.0162	0.0090	0.0053	0.0024	0.0167
7	0.0051	0.0061	0.0021	0.0133	0.0051	0.0054	0.0022	0.0126
8	0.0018	0.0103	0.0027	0.0148	0.0047	0.0181	0.0022	0.0250

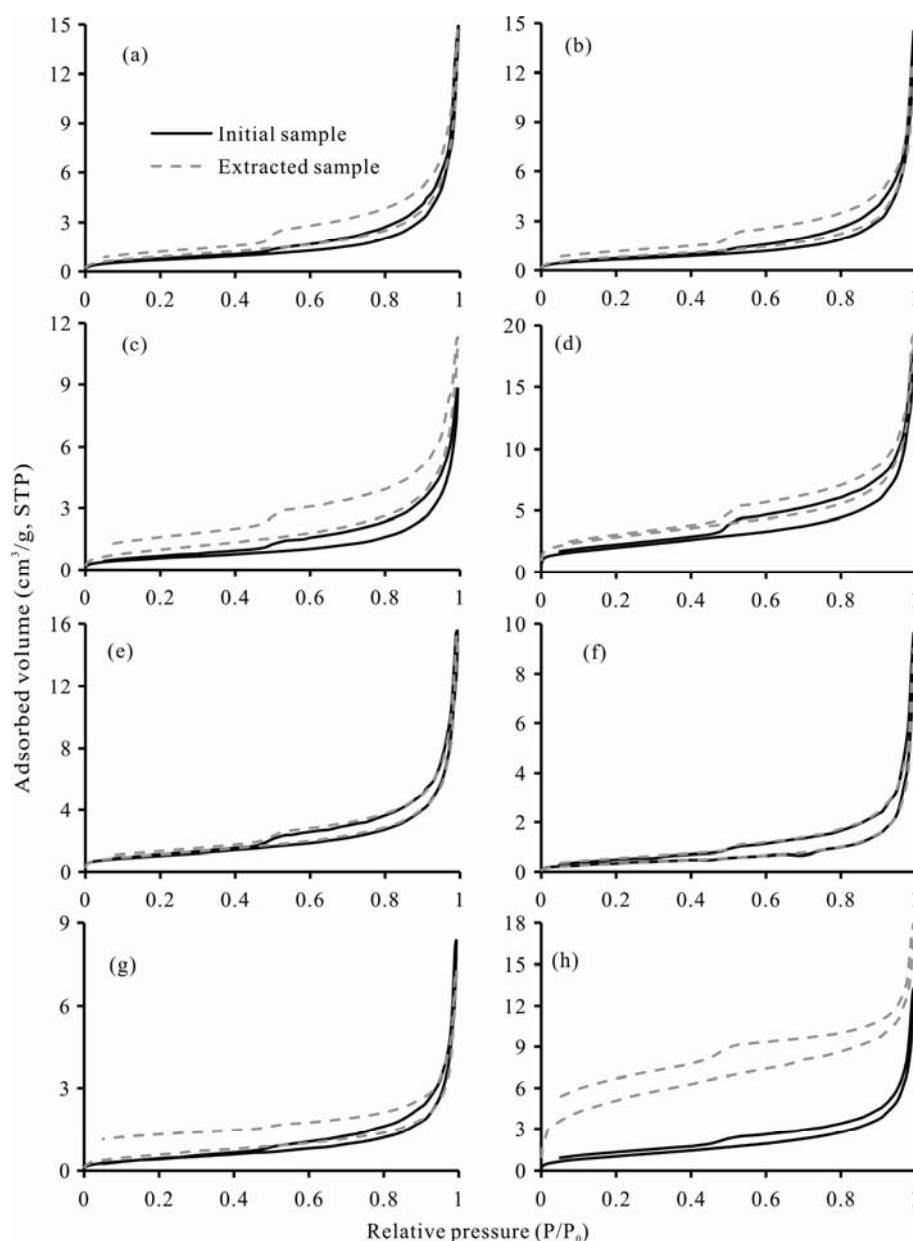
Fig. 7. Low-pressure N₂ adsorption isotherms for the studied samples.

Table 6 Surface area data of the extracted samples

Sample	Initial samples (m ² /g)				Extracted samples (m ² /g)			
	Micropore	Mesopore	Macropore	Total	Micropore	Mesopore	Macropore	Total
1	1.71	2.47	0.19	4.38	1.71	2.97	0.19	4.87
2	3.03	2.32	0.22	5.56	3.03	2.63	0.16	5.82
3	5.78	1.91	0.12	7.81	9.92	3.09	0.16	13.17
4	5.89	5.38	0.22	11.49	8.04	6.74	0.23	15.02
5	6.82	3.24	0.25	10.31	6.82	3.36	0.28	10.46
6	21.63	1.19	0.15	22.97	24.79	1.16	0.15	26.10
7	14.65	1.40	0.13	16.19	14.65	1.65	0.13	16.44
8	4.85	3.23	0.17	8.24	14.49	12.75	0.14	27.38

nm, respectively. For the initial samples, the micropore, mesopore, and macropore volumes are in the ranges of 0.0004–0.0079, 0.0059–0.0162, and 0.0019–0.0040 cm³/g respectively, and their surface areas are in the ranges of 1.71–21.63, 1.19–5.38 and 0.12–0.25 m²/g, respectively.

For the extracted samples, the corresponding ranges of pore volumes are 0.0004–0.0090, 0.0053–0.0181 and 0.0022–0.0046 cm³/g, and the corresponding ranges of surface areas are 1.71–24.79, 1.16–12.75 and 0.13–0.28 m²/g, respectively.

Figures 8 and Figure 9 show complex changes in pore volume and surface area between the initial and extracted samples. For some of the samples, the micropore volume is similar between the extracted and initial samples (Fig. 8a). The micropore volumes of samples 3, 4, 6 and 8 clearly increase after extraction (Fig. 8a). The surface area of the micropores shows similar variations to the micropore volume after extraction (Fig. 9a). The mesopore volumes of samples 1, 3, 4 and 8 increase after extraction (Fig. 8b), while other samples show the opposite trend. For the surface area of the mesopores, only sample 6 has lower values after extraction (Fig. 9b). For samples 1, 2 and 8, the macropore volume of the extracted samples is less than that of the initial samples (Fig. 8c); the other samples show a normal trend. For samples 2 and 8, the surface area of the macropores in the extracted samples is smaller than that in the initial samples (Fig. 9c). The other samples show the opposite trend (Fig. 9c). For samples 2 and 7, the total pore volume of the extracted samples is smaller than that of the initial sample (Fig. 8d), whilst the opposite trend is found for the other samples. All samples show a higher total surface area after extraction (Fig. 9d). The abnormal changes described above may be attributable to some of the pores in initial samples having become larger ones, making the pore volumes and surface areas of the pores within mesopore or macropore diameter range decrease.

4.5 Pore size distribution

The pore size distribution (PSD) was calculated for each sample using the LPGA-CO₂ and LPGA-N₂ data (Fig. 10). For most of the samples there are two major peaks at pore size diameters of 0.6 and 0.8 nm (Fig. 10), whereas samples 4 and 8 show three major peaks at 0.6, 0.8 and 6 nm (Fig. 10d, j). For samples 1, 2, 3, 7 and 8, the PSD lines of the extracted samples are higher than those of the initial samples (Fig. 10a–c, h–i). For other samples, the PSD lines before and after extraction are similar.

5 Discussion

As shown in Fig. 8, all the studied samples showed a larger or similar micropore volume than the initial ones. However, the variations in mesopore and macropore volumes are complex after extraction. For some samples, their mesopore or macropore volumes are smaller than the initial ones. It is possible that extraction makes some of the mesopores and macropores become larger, resulting in the reduction of mesopore or macropore volumes.

A strong positive relationship between micropore volume and TOC content can be seen in Figure 11a–b, which suggests that the micropores develop mainly in

organic matter. Similar correlations have been reported for many other shales, such as the Lujiaping shales (Han et al., 2016a), the Muskwa shales (Ross and Bustin, 2009), and the Marcellus shales (Milliken et al., 2013). However, there is no obvious relationship between TOC content and pore volume in the New Albany shale (Mastalerz et al., 2013), which may be related to differences in organic matter type and mineral composition between the New Albany shale and our samples. In contrast, mesopore and macropore volume show negative correlations with TOC content (Fig. 11c–f). No obvious correlations exist between mesopore and macropore volumes and the amounts of clay minerals, quartz and feldspar. According to the correlations above, we speculate that the mesopores and macropores in the studied samples develop in fractions other than organic matter. The poor correlations between pore volume and mineral compositions suggest that the effects of mineral compositions are masked by the stronger influence of TOC content.

Figure 12 shows the variations of TOC content, S₁, micropore volume, mesopore volume, and macropore volume with increasing maturity. With the increase of vitrinite reflectance, TOC content increased (0.64%R_o–0.84%R_o) firstly and then decreased, which is opposite to the normal trend, indicating the original TOC content of the studied samples varies across a wide range. The obvious difference in TOC content of the studied samples can be attributed to the wide distribution of sampling locations shown in Fig. 1. The variation trend of micropore volume is consistent with TOC content, while mesopore and macropore volume has an inverse trend. The variations of pore volumes and TOC content agree well with the correlations between them shown in Fig. 11. Therefore, TOC content is a stronger controlling factor of pore development in our studied samples. The influences of maturity, mineral composition and compaction are all masked by it.

The samples extracted using dichloromethane show a similar trend with TOC content and vitrinite reflectance to the initial samples (Fig. 12). Accordingly, we speculate that the EOM in the studied shale samples was mainly stored in the pores beyond the detection range (0.3–80 nm) of low-pressure gas adsorption experiments. The oil in the detectable pores cannot be easily extracted using dichloromethane. In addition, the utilized particle size (60 mesh) is coarser than in the standard (80 mesh, SY/T 5118–2005), which may also be responsible for the low extraction efficiency. Therefore, EOM shows a weaker effect on pore development than TOC content. The pore volume of some of the samples did not increase after extraction (e.g., samples 2 and 7). It is noteworthy that Wei et al. (2014) found that extraction with toluene

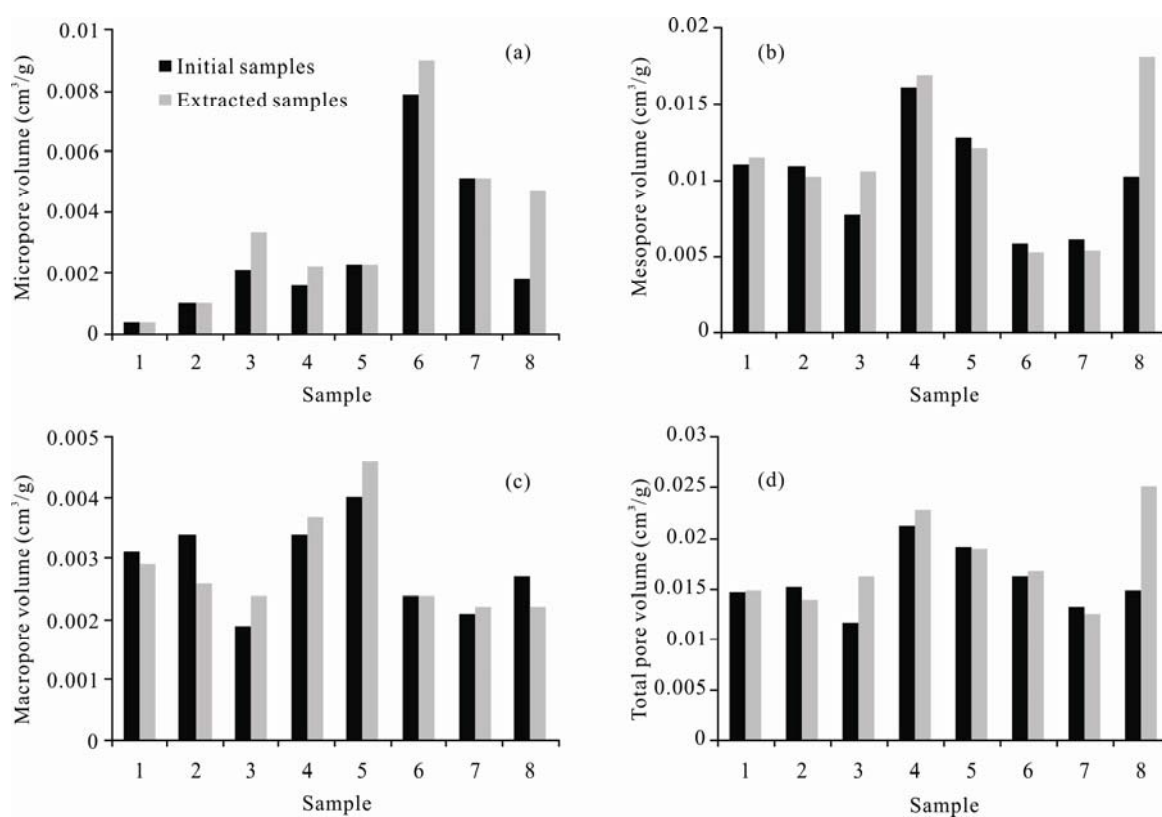


Fig. 8. Histograms of pore volume for the studied samples.

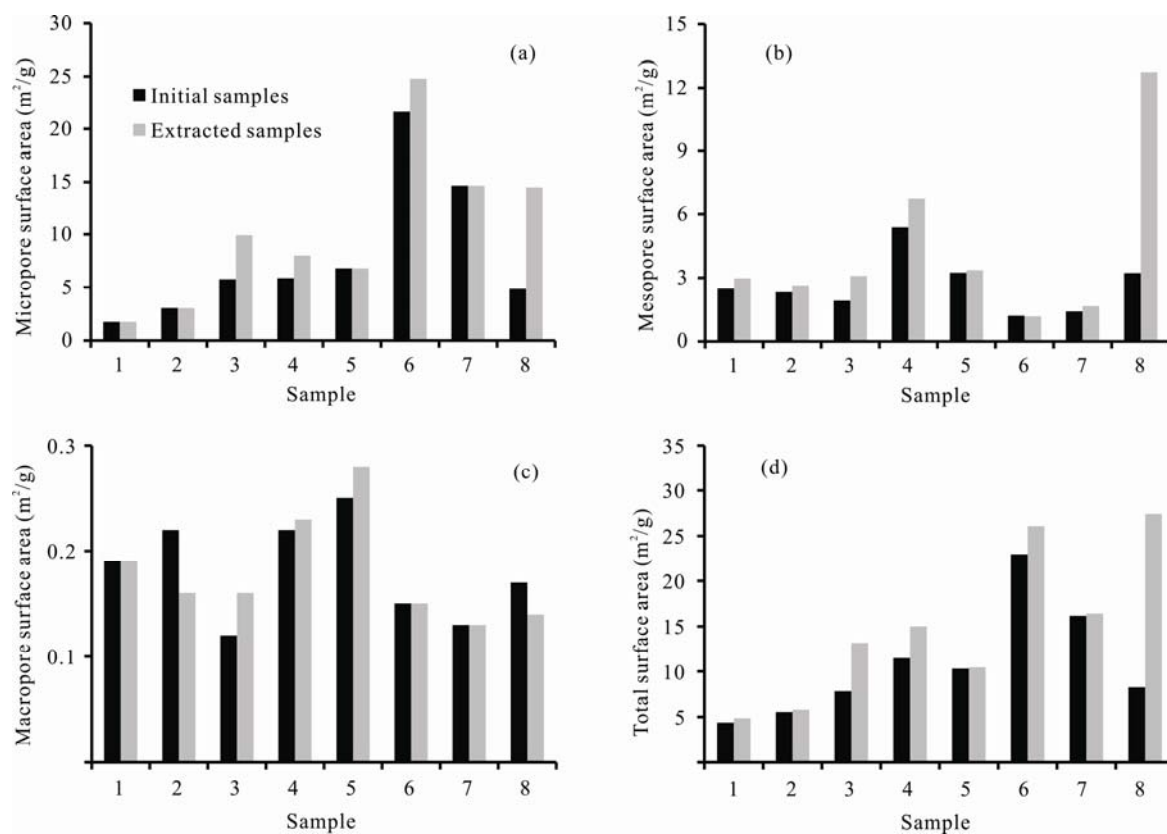


Fig. 9. Histograms of surface area for the studied samples.

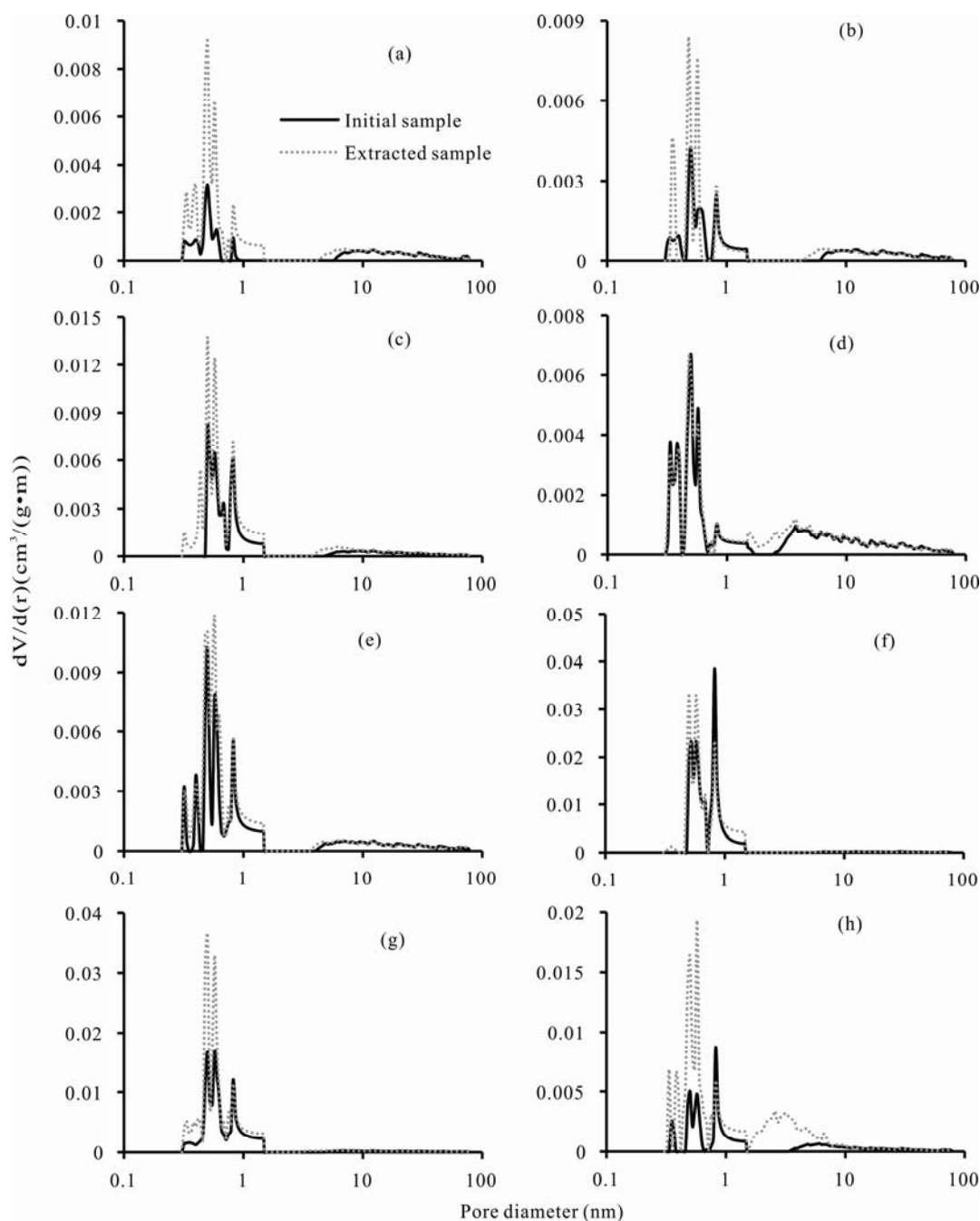


Fig. 10. Pore size distributions of the studied samples.

increases the pore volume of shales much more than extraction with dichloromethane. This phenomenon can be explained by the higher boiling point of toluene (111°C) relative to dichloromethane (39.6°C), which enhances its dissolution of bitumen. Accordingly, to identify the influence of retained oil on pore development, extraction should be conducted using an organic solvent with a higher boiling point in future studies.

6 Conclusions

To explore the influence of EOM on pore development

in lacustrine shales, a suite of mature shale samples was chosen from the Chang 7 member of the Triassic Yanchang Formation in the Ordos Basin, China. Soxhlet extraction was performed on the samples using dichloromethane. Low-pressure gas (CO_2 and N_2) experiments were conducted on the samples before and after extraction. The results show that pore development is mainly controlled by TOC content for both the initial and extracted samples. The correlations between pore volume and TOC content indicate that micropores mainly developed in organic matter, while mesopores and macropores dominantly developed in fractions other than

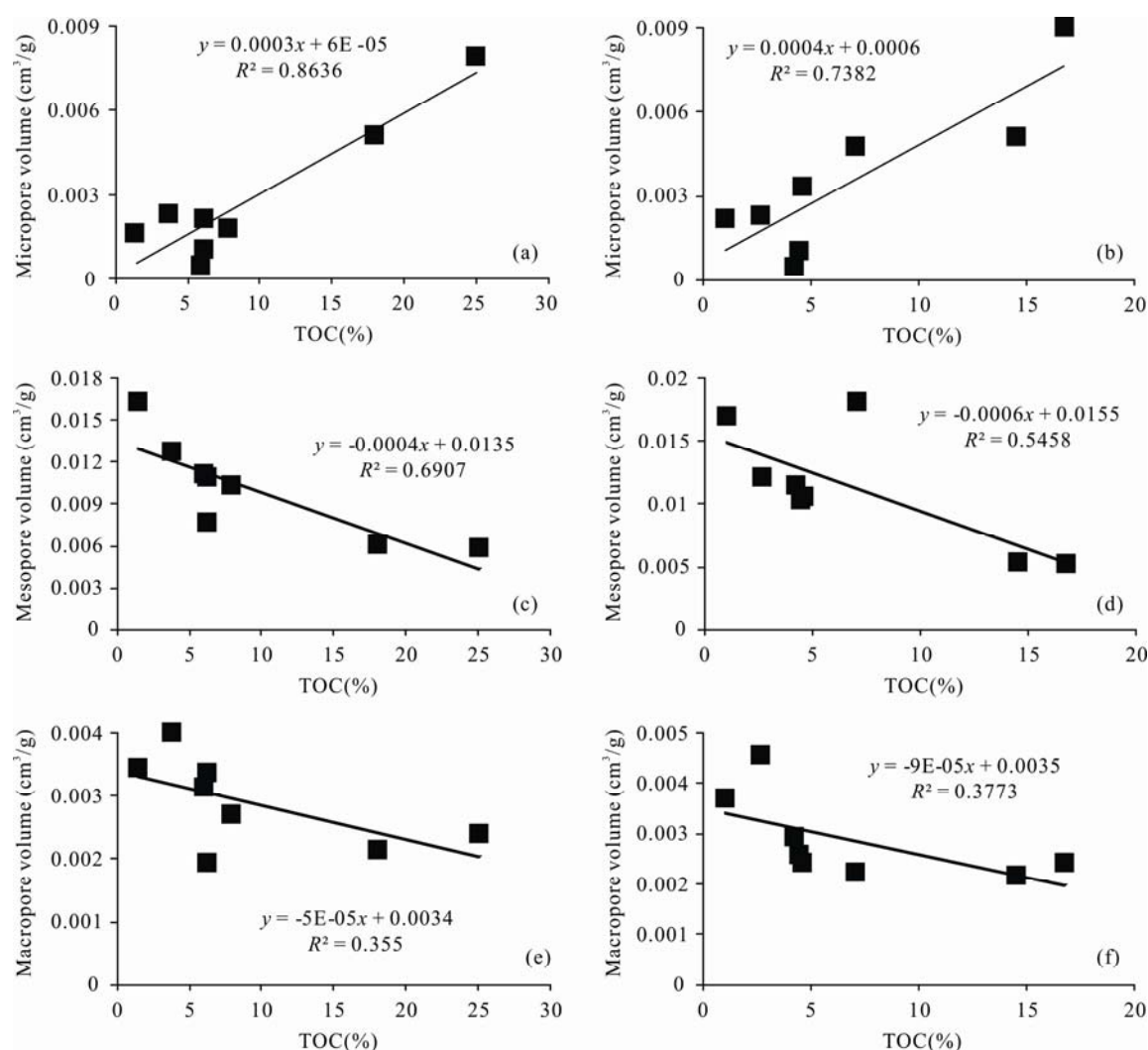


Fig. 11. Relationship between TOC and pore volume for the studied samples.
(a, c, and e show the initial samples; b, d, and f show the extracted samples.)

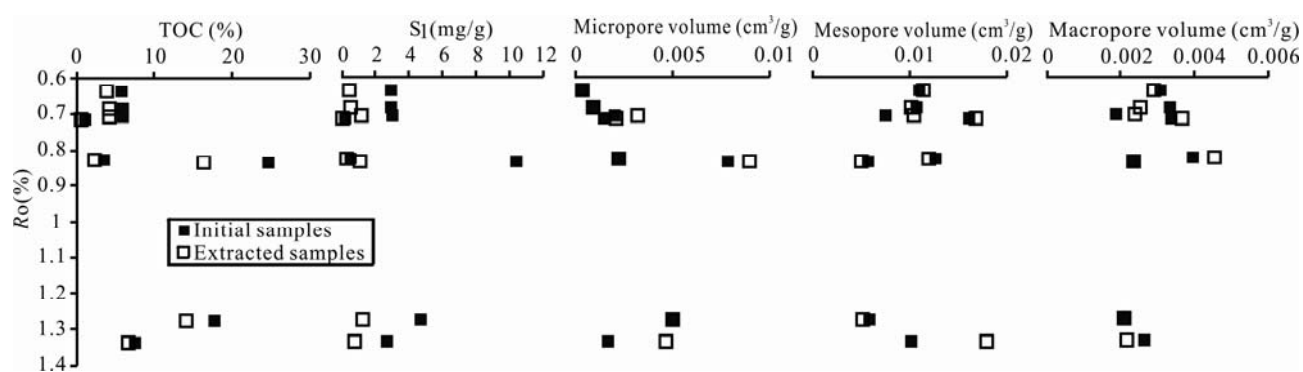


Fig. 12. Geochemical data and pore volume vs. R_0 for the studied samples.

organic matter. The influence of maturity on pore development needs to be investigated by choosing samples with various maturity levels but similar organic and inorganic compositions.

In addition, we speculate that the extractable organic

matter in the studied samples cannot be effectively extracted by dichloromethane. Extraction should be conducted using an organic solvent with a higher boiling point in the future. Finally, owing to the small numbers of samples and the wide distribution of sampling locations,

our conclusions need to be viewed with some degree of caution.

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