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Research paper

# Geochemical characterization and quantitative evaluation of shale oil reservoir by two-dimensional nuclear magnetic resonance and quantitative grain fluorescence on extract: A case study from the Qingshankou Formation in Southern Songliao Basin, northeast China



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#### ABSTRACT

Understanding the content and geochemical characteristics of shale oil are two significant aspects of shale oil exploration and evaluation. This paper details the analysis of 32 shale samples extracted by sealed coring from the first member of the Upper Cretaceous Qingshankou Formation (K2qn<sup>1</sup>) in the Southern Songliao Basin, northeast China. Geochemical techniques including Rock-Eval pyrolysis, contents of total organic carbon (TOC) and clay mineral identification by X-ray diffraction (XRD) were performed on the samples. A total of 13 samples were further analyzed using two-dimensional nuclear magnetic resonance (2D NMR) and the quantitative grain fluorescence on extract (QGF-E) technique to determine the content and properties of different types of organic matter (OM) in the shale reservoir. The OM content and spectral intensity obtained from the NMR and OGF results were positively correlated with TOC content and pyrolysis  $S_1$  of the samples, respectively. In addition, the characteristic fluorescence parameters  $(R_1, R_2)$  of the shale extract and crude oil obtained by total scanning fluorescence (TSF) indicated that the crude oil in the studied shale reservoir was a thick-medium oil in the medium mature stage. The comprehensive experiment with the combined use of high-frequency 2D NMR and QGF technologies realized the quantitative characterization of shale oil composition and maturity, and demonstrated advantages of nondestructive, rapid and quantitative detection of OM, especially oil content in shale. New shale oil evaluation parameters obtained from these experiments, therefore, are more significant than traditional measurements such as Soxhlet extraction and pyrolysis.

# 1. Introduction

Since the beginning of the 21st century, shale oil and gas classified as unconventional oil and gas resources have increasingly become more significant in the international energy market. According to data released by the United States Energy Information Administration in 2013, China's shale oil resources have vast potential with 32.2 billion barrels of recoverable resources given the current shale oil technology in China (EIA U.S., 2013).

In contrast to the successfully commercialized marine shale series in the United States, continental shale in China is characterized by relatively low organic matter (OM) content, low maturity, high clay minerals content, and significant heterogeneity. In addition, China's continental shale oil is still in its primary developmental stage and is fraught with various unresolved challenges. Amongst others, content and geochemical characteristics of shale oil are two critical aspects for the evaluation of the economic development potential of shale oil resources (Jarvie, 2012; Liu et al., 2012).

Common indexes used to characterize shale geochemical properties, and shale oil content mainly include total organic carbon (TOC) content determined by elemental analyzer, chloroform asphalt "A" obtained by Soxhlet extraction,  $S_1$  and oil saturation index (OSI) (OSI =  $S_1$ / TOC × 100) obtained by Rock-Eval pyrolysis (Liu et al., 2016, 2019; Curiale and Curtis, 2016). However, these conventional experimental

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methods are relatively limited as they are based on the evaluation of the source rock. In the application of these methods, the interpretation of each parameter during the preservation, pretreatment and experiment of a sample is not directly related to the recoverable crude oil content in the shale reservoir. For instance, the programmed temperature in the pyrolysis experiment inevitably leaves out part of the light-medium hydrocarbon components ( $C_{17}$ ) from the  $S_1$  measurement results. Furthermore, the chloroform asphalt "A" not only lacks some light hydrocarbons but also contains an abundance of invalid heavy components (like colloid and asphaltene), which are difficult to mine in actual development (Liu et al., 2014a). Generally, the hydrocarbon expulsion threshold of source rocks occurs at approximately OSI > 100 mg HC/gTOC, which is also considered to be the boundary of the mining value for marine shale reservoirs (Pepper, 1991; Jarvie, 2012). This is comparative to the continental shale reservoir with low oil content, considered to have a mining value of OSI > 75 mg HC/g TOC (Xue et al., 2015). In petroleum exploration, nuclear magnetic resonance (NMR) is widely used to obtain various parameters such as porosity, pore size distribution and permeability of rock samples. However, the moderate sensitivity of the conventional low frequency (2 MHz) NMR restricts quantitative identification of crude oil, pore water and solid organic matter of shale reservoirs thus limiting the application of this technology in shale oil and gas evaluation (Birdwell and Washburn, 2015).

In contrast, the recently developed high frequency (23 MHz) 2D NMR can identify and quantify different properties of OM and fluids in shale reservoirs using the high frequency 2D NMR  $T_1$ - $T_2$  map. The results of high frequency 2D NMR also have a good correlation with the parameters obtained from pyrolysis experiments (Khatibi et al., 2019). Furthermore, quantitative grain fluorescence on extract (QGF-E and TSF) with merits of quantitative and whole rock detection has been widely used in conventional reservoir oil and gas filling history and (ancient) reservoir identification (Liu and Eadington, 2005), but no related tests have been carried out in the evaluation of the oil-bearing property of shale reservoirs.

In this study, we selected shale samples extracted via sealed coring thus preserving in-situ properties. One crude oil sample was obtained from the target shale formation. The geochemical characteristics of shale and the content and properties of oil in the shale reservoir were then studied using conventional geochemical analyses such as TOC content and Rock-Eval pyrolysis, as well as high-frequency (23 MHz) 2D NMR and QGF techniques. The study provides new parameters and ideas for unconventional shale oil and gas evaluation.

#### 2. Geological setting

The Songliao Basin, located in Northeast China, lies the NE-NNE direction. It is one of the largest oil-bearing basins in China, covering an area of approximately  $2.6 \times 10^5 \,\mathrm{km^2}$  and extending  $7.5 \times 10^4 \,\mathrm{m}$  in length and  $(3.3–3.7) \times 10^4 \,\mathrm{m}$  in breadth (Fig. 1a). According to the basement and tectonic development characteristics in the study area, the Songliao Basin can be divided into six first-order tectonic units, namely northern plunge, western slope, southwestern uplift, southeastern uplift, northeastern uplift, and central depression (Fig. 1b; Liu et al., 2019). Considering Songhua River, Nen River and Lalin River as the boundary, Songliao basin can be divided into two parts: the northern part is the exploration area of Daqing oilfield, and the southern part is the exploration area of Jilin oilfield. The Jilin exploration in the southern part of the central depression can be further divided into four secondary tectonic units: Honggang terrace, Changling sag, Fuxin uplift belt, and Huazijing terrace.

For this study, the sampling well is located in the northern part of the Changling sag (Fig. 1c). From bottom to top, the primary drilling layer is composed of the Lower Cretaceous Quantou Formation, the Upper Cretaceous Qingshankou and the Yaojia Formations (Fig. 1d). The Qingshankou Formation ( $K_2qn$ ) is divided into three members. The first member of the lowermost Qingshankou Formation (abbreviated as Qing-1 member,  $K_2qn^1$ ) is the cored layer. During the  $K_2qn^1$  deposition, the basin, which is characterized by lacustrine expansion, formed a set of widely distributed OM-rich continental shale (Liu et al., 2019). According to hundreds of shale samples of the Qing-1 member reported by Liu et al. (2017) and Liu et al. (2019), most shale samples have characteristic high organic matter content (TOC content ranges from 0.12 to 7.48 wt% with a mean of 2.26 wt%), and kerogen is mainly type I with some type II. Furthermore, both  $T_{max}$  and Ro values ( $T_{max}$  value ranges from 435 to 463 °C and Ro value ranges between 0.41 and 1.27%) indicate that organic matter of Qing-1 member is within hydrocarbon generation window. Presently, this formation is in the mature stage of oil generation within the study area and thus is the main source of conventional oil and gas reservoirs and a favorable target for shale oil exploration (Liu et al., 2019).

#### 3. Experimental methods

For the experiments, a total of 32 shale samples were selected from the first member of the Qingshankou Formation in the northern Changling sag. The samples were retrieved following systematic sealed coring ensuring maximum preservation of the original fluid in the shale. Basic tests like XRD analysis, TOC content measurements and Rock-Eval pyrolysis were performed on all shale samples. Following analysis of the results from these measurements, 13 shale samples with significant differences in pyrolysis parameters were selected for further analyses using high-frequency 2D NMR and QGF techniques, while TSF was performed on a crude oil sample from Qing-1 member.

## 3.1. Mineral composition and bulk geochemical parameters

Crystals of different minerals have specific X-ray diffraction patterns. The intensity of each characteristic peak of the pattern is proportional to the abundance of the mineral in the sample, thereby determining the mineral composition in the sample by the D/max-2200-Xray diffractometer ingredient. The TOC content was determined by first using dilute hydrochloric acid to strip the sample of inorganic carbon. Organic carbon in the sample was then converted to CO<sub>2</sub> by burning the sample in a high-temperature oxygen stream using a CS-230 analyzer, followed by ascertaining the TOC value with an infrared detector. Geochemical parameters measured using Rock-Eval 6 included  $S_1$ ,  $S_2$ , and the temperature of maximum pyrolysis yield,  $T_{\text{max}}$ .  $S_1$  was measured at 300 °C for 3 min, and  $S_2$  was measured after the temperature was programmed to increase to 550 °C.  $T_{\rm max}$  was determined as the pyrolysis temperature corresponding to the highest point of the  $S_2$  peak response. The hydrogen index (HI) is expressed as  $S_2$ /TOC × 100, and the oil saturation index (OSI), is given as  $S_1$ /TOC × 100, where,  $S_1$  and  $S_2$  represent the sample residual hydrocarbon content and pyrolysis hydrocarbon content, respectively.  $T_{\max}$  exhibited a good correlation with the maturity of the source rock.

#### 3.2. Two-dimensional nuclear magnetic resonance of high-frequency

A high-precision NMR instrument, MR Core-XX, with an experimental frequency of 23 MHz and produced in the United States, was used in this experiment. The instrument, equipped with a 30 mm diameter probe, reduced the acquisition dead time to as low as  $15 \,\mu s$  enabling the measurement of the minimum T<sub>2</sub> response of the solid organic matter in the shale. In addition, the Carr-Purcell-Meiboom-Gill (CPMG) pulse sequence was used to obtain the transverse relaxation time, T<sub>2</sub>. The CPMG pulse sequence has the advantage of overcoming the influence of the internal magnetic field and is more suitable for experimental processes than the free induction decay (FID) sequence. The FID sequence was generally used in the debugging phase of the instrument. The echo interval (TE) of 0.07 ms is used to detect the fluids in the nanopores and the solid organic matter. The longitudinal relaxation time, T<sub>1</sub>, was measured using the industry-wide inversion



Fig. 1. Location (a) along with six tectonic units maps of the Songliao Basin (b), and the study area (c). General lithologic stratigraphy of Changling sag (d) (modified from Liu et al., 2019).

recovery (IR) sequence. Different rock samples (for example, carbonate and shale) required specific experimental parameter settings for optimal results. At the start of the test, the instrument was calibrated with standard vegetable oil of known volume before the weighed original shale sample was placed in a 30 mm diameter sample tube. The transverse relaxation time of  $T_2$  was measured to obtain all the <sup>1</sup>H (Protium) rich fluid content (Bloembergen et al., 1948) in the sample, followed by the 2D NMR detection of longitudinal relaxation time, T<sub>1</sub>, and transverse relaxation time, T<sub>2</sub>. For the T<sub>1</sub>-T<sub>2</sub> data acquisition, T<sub>1</sub> used 61 equal steps, each of which recorded 5000 echoes. Finally, the Optimized Truncated Singular Value Decomposition (OTSVD) inversion was used to obtain the T1-T2 map which reflects the fluid distribution (Hanson, 1971; Hansen, 1987). <sup>1</sup>H in the rock matrix did not contribute to the signal response (Slijkerman et al., 2001). The solid organic kerogen and asphaltenes had larger T<sub>1</sub> values and lower T<sub>2</sub> values, due to the low efficiency of solid organic matter transmitting fluctuating energy to the environment and the strong intramolecular polar coupling. Inorganic OH-(hydroxyl), clay minerals bound water, free water in nanopores or cracks had small T1 values. The magnitude of the T2 value reflects the fluidity of the <sup>1</sup>H-rich material (for example, kerogen, asphaltene, water, light oil) in the porous medium. The higher the  $T_2$ value, the lower the fluidity and the higher the viscosity of the fluid (Khatibi et al., 2019). This principle guided the identification of the movable oil distribution interval in the T<sub>1</sub>-T<sub>2</sub> map.

# 3.3. Quantitative grain fluorescence on extract

A Varian Cary-Eclipse photometer was used to detect the fluorescence properties of the adsorbed hydrocarbon extract on the shale reservoir particle surface based on QGF-E and total scanning fluorescence (TSF). For the QGF-E measurement, a 260 nm excitation light with an emission range of 300-600 nm was used, while a 220-340 nm excitation wavelength with an emission wavelength range of 250-540 nm was used for the TSF measurement. A 0.1 g 80-100 mesh sized shale

sample was placed in a 50 ml beaker to which 20 ml dichloromethane (DCM) was added and set to oscillate for 15 min. The oscillation was repeated twice for 15 min at 10 min intervals. After a standing time of 1 h, the supernatant was collected for quantitative fluorescence analysis of the hydrocarbons adsorbed on the shale reservoir particles surfaces. Prior to each measurement, a DCM blank sample was tested to ensure that the quartz cuvette was clean and the fluorescence intensity less than 10 photometer count (pc). This prevented interference of the solvent DCM with the test results and facilitated deduction of the signal response contribution from the experiment results. The QGF-E pre-experiment was performed before the TSF experiment, guaranteeing that the maximum emission wavelength did not exceed the detection limit (while ensuring that the sample did not undergo fluorescence quenching). In cases where the detection limit was exceeded, the diluted multiples were recorded, with which the results were normalized to the standard set of a 1 g shale sample particle to 20 ml DCM extract. The normalized QGF-E intensity is determined as the maximum fluorescence intensity value after normalization.  $\lambda_{max}$  is the emission light wavelength corresponding to the QGF-E maximum intensity and is a parameter that reflects the viscosity and composition of the crude oil (Liu and Eadington, 2005). TSF maximum intensity (TSF-Max), maximum excitation wavelength (MAX-EX), maximum emission wavelength (MAX-EM), R1 and R2 are used to determine the spectral characteristics of TSF (Liu et al., 2014b). The maximum intensity of TSF corresponds to the intensity of QGF-E, which is the maximum intensity in the normalized TSF spectrum. MAX-EX and MAX-EM are the excitation and emission wavelengths corresponding to the maximum intensity of the TSF. R1 is the ratio of the fluorescence intensity of the emission wavelength at 360 nm to the fluorescence intensity of the emission wavelength at 320 nm as the excitation wavelength is 270 nm. R<sub>2</sub> is the ratio of the fluorescence intensity at the emission wavelength of 360 nm to the fluorescence intensity of the emission wavelength of 320 nm as the excitation wavelength is 260 nm. Α

positive correlation exists between the maximum TSF



Fig. 2. (a) Triangular plot of whole rock mineral composition in the first member of Qingshankou Formation. (b) Bar graph of clay mineral content.

fluorescence intensity and the shale oil saturation, indicating that unknown parameters can be solved from known parameters (Liu, 2018). In this study, we prepared the standard solution of different oil content and then measured the related TSF fluorescence intensity. For the calculation process of oil saturation within shales, the density and the porosity of the shale samples are constant values ( $2.55 \text{ g/cm}^3$  for density and 4.5 vol% for porosity). In order to get more accurate calculation results, it is better to measure the density and porosity of each sample separately.

#### 4. Experimental results and explanation

## 4.1. Mineral composition

The mineral composition of the continental shale within the Qing-1 member is characterized by complexity and significant heterogeneity (Fig. 2). The mineral composition mainly includes quartz (ranging from 19.1 wt% to 44.7 wt%, average 34.9 wt%), clay minerals (ranging from 14.0 wt% to 54.4 wt%, average 33.9 wt%), and feldspar (ranging from 3.1 wt% to 27.8 wt%, average 7.9 wt%), whereas the carbonate content is low (at 0–56.3 wt%, average 10.6 wt%). Feldspar is dominated by plagioclase (3.1 wt% - 27.8 wt% and average 3.3 wt%), K-feldspar was detected in only two samples (at 0.7 wt% and 2.2 wt%). The carbonate minerals are mainly Fe-dolomite, with an average content of 8.2 wt%. Most samples contain little or no calcite (average 2.4 wt%). Siderite and pyrite are common. Most of the samples have a siderite content of more than 3.0 wt%, with an average of 3.7 wt%, and a pyrite content of 0.4 wt% to 9.5 wt%, with an average of 3.6 wt% (Table 1).

Mesodiagenesis can be divided into two sub-stages. Conversion of smectite to illite and clay mineral dehydration occurs during the whole mesodiagenesis stage. The illite and illite-smectite (I/S) mixed layers are two important characteristic minerals which dominate the mesodiagenesis stage, with the late mesodiagenesis substage the main phase of hydrocarbon genesis (Foscolos et al., 1976). In this study, the clay minerals are mainly composed of illite and I/S mixed layers, with a small amount of chlorite, indicating that the rock is in the Mesodiagenesis stage, from the end of early mesodiagenesis to the beginning of late mesodiagenesis. The illite and I/S mixed layers range from 56 wt% to 88 wt% (average of 73.6 wt%) and 10 wt% to 32 wt% (average of 17.6 wt%), respectively. The chlorite content is up to 12 wt% with an average of 4.8 wt%, while Kaolinite is less abundant, with most occurrences below 10 wt%.

#### 4.2. Geochemical characteristics

The results of TOC content and Rock-Eval pyrolysis are shown in Table 1. The TOC content of the Qing-1 shale in the Southern Songliao Basin varies between 0.97 wt% and 7.27 wt%, with an average of 3.30 wt%. The samples with TOC content more than 2.0 wt% account for 54.4% of the total.  $S_1$  varies between 0.66 and 2.46 mg HC/g with an average of 2.50 mg HC/g. The value of  $S_2$  varies widely, with an average of 23.81 mg HC/g of 5.0–54.5 mg HC/g. HI varies between 509 and 897 mg HC/g TOC. OSI ranges from 29 to 86 mg HC/g TOC with the high values concentrated in the depth range of 1530 m–1537 m. Given the mature stage of the shale which coincides with the diagenetic stage determined by clay minerals, the  $T_{max}$  has a small range of 440–455 °C. This indicates that the OM in the target interval has reached the stage of maturity and has begun to generate large amounts of hydrocarbons. This interpretation is consistent with the characteristics of the mesodiagenesis stage.

The plot of HI and  $T_{\text{max}}$  indicates that the OM type of the Qing-1 shale is dominated by type I kerogen (Espitalié et al., 1984, Fig. 3a).  $S_2$  has a good linear correlation with TOC content, with the correlation coefficient R<sup>2</sup> reaching 0.94, which indicates that the OM type of the shales has a good degree of homogeneity, with original HI of 796 mg HC/g TOC (Langford and Blanc-Valleron, 1990, Fig. 3b).  $S_1$  and TOC values have a positive correlation, pointing to the role of the kerogen as the base of the raw oil. As TOC content > 2.0 wt%,  $S_1 > 1.0$  mg HC/g and as TOC content < 1.0 wt%,  $S_1 < 0.5$  HC mg/g (Fig. 3c).

# 4.3. QGF-E and TSF results

QGF-E and TSF (Table 2) characterize parameters of the Qing-1 member shale samples, including the maximum TSF fluorescence intensity of the extract and the normalized QGF-E and TSF parameters. The QGF-E fluorescence spectrum shows the unimodal characteristics of the overall shift to the left, and the  $\lambda_{max}$  of different samples is evenly distributed at about 380 nm. These prove that the composition of shale oil in the Qing-1 member is relatively uniform (Fig. 4). Compared to the fluorescence spectra of different crude oils and hydrocarbons (Liu and Eadington, 2005), the shale oil of the Qing-1 member is a thick-medium oil with a slightly higher viscosity.

Number	Depth (m)	) Rock-Eve	ıl.					Whole Ro	ock Mineralo,	gy (wt.%)					O	ay (Phyllos	ilicate) Mine	eralogy (wt.%)	
		TOC (wt.%)	T <sub>max</sub> (°C)	S <sub>1</sub> (mg HC/g)	S <sub>2</sub> (mg HC/g)	OSI (mg HC/g)	HI (mg HC/ g TOC)	Quartz	K-feldspar	Plagioclase	Calcite	(Fe-) Dolomite	Siderite 1	Pyrite T	otal Clay Ill	ite kaolin	ite chlorite	e Chlorite/ Smectite	Illite/ Smectite
1	1483.46	1.78	447	0.7	11.4	37.0	641	31.8	0	16.5	0	0	1.0 0	5.3 4	4.5 82	0	2	0	16
2	1484.30	6.93	455	2.0	54.5	29.4	786	37.2	0	27.8	0	3.3	2.0	4.3 2	5.4 78	0	4	2	16
co	1488.25	2.83	448	1.6	24.0	57.6	848	36.4	0	19.1	0	3.0	1.0	4.8 3	5.7 7.	0	4	0	19
4	1491.77	3.64	446	1.7	25.9	47.5	710	39.9	0	18.9	0	2.3	4.7	3.3 3.	0.9 75	0	9	0	19
ß	1492.50	1.99	446	0.8	12.1	41.3	608	31.0	0	14.6	0	9.7	1.1	3.0 4	0.5 78	0	ĉ	0	19
9	1494.11	4.17	447	2.3	28.8	55.7	692	34.1	0	18.5	0	1.3	6.7	4.0 3	5.4 7.	0	2	0	21
7	1497.08	2.22	447	1.2	13.6	53.6	611	31.4	0	18.1	4.2	1.0	6.5	3.7 3	5.0 72	0	7	0	21
8	1497.84	3.98	450	1.7	27.6	41.7	692	36.5	0	21.1	2.4	3.0	2.5	4.5 3	0.0 75	0	7	0	18
6	1500.84	3.59	448	1.3	24.6	37.1	686	39.4	0	15.1	4.7	1.2	2.3	3.7 3	3.7 79	0	ß	0	16
10	1503.01	2.21	442	1.3	12.8	57.0	581	35.3	0	16.5	4.7	4.9	3.8	2.7 3	1.9 70	0	ĉ	0	21
11	1505.31	2.32	442	1.7	13.9	71.9	598	32.2	0	15.2	17.1	1.2	6.2	1.9 2	6.2 69	9 (	7	0	18
12	1507.84	2.80	451	1.2	23.7	43.6	846	37.5		3.1	7.9	2.9	5.0	5.1 3	7.5 88	0	2	0	10
13	1509.70	3.52	451	1.0	26.2	29.2	744	35.6	0	16.1	3.4	1.1	3.5	5.9 3	4.5 8(	0	2	0	12
14	1511.48	2.52	448	1.2	20.5	45.6	811	23.0	~ 0	8.2	0	37.9	2.4	2.5 2	5.9 57	, 23	9	0	14
15	1513.28	4.12	448	1.2	30.9	29.2	750	35.6	0	15.9	0	0.8	15.3 (	0.8 3	1.5 69	7	7	0	17
16	1516.15	3.12	450	1.1	21.5	34.6	689	37.9	0	14.6	0	7.6	1.5	5.0 3	2.4 7.	0	4	0	19
17	1516.50	2.84	451	1.0	21.8	36.6	768	38.1	0	15.8	0.3	0.9	3.0	5.8 3	5.1 8!	0	1	0	14
18	1518.43	3.25	451	1.3	24.4	40.0	751	35.3	2.2	21.0	0.3	3.1	3.6	5.3	9.3 8.	0	4	0	13
19	1520.35	4.44	451	1.9	39.8	42.4	897	28.8	0	7.3	2.3	2.6	1.5	3.2 5	4.4 7/	9	9	0	14
20	1523.300	3.01	449	1.5	25.6	48.2	849	19.1	, 0	4.4	0	32.3	1.8	2.2 4	0.2 75	9	4	0	15
21	1525.62	5.27	453	1.7	42.1	32.5	299	43.3	0	10.7	0	1.3	3.9	3.4 3	7.4 68	9 6	9	0	20
22	1527.41	4.17	449	1.9	33.8	46.1	812	43.2	0	10.2	0	1.9	4.1	4.3 3	6.3 64	10	7	0	19
23	1528.09	4.33	451	1.6	31.5	36.7	726	44.7	0	11.2	0	2.2	3.5	0.4 3	8.0 69	8	5	0	18
24	1529.59	2.81	450	1.7	18.8	61.2	668	41.9	0	13.4	0	0.7	2.8	2.7 3	8.5 7(	5	9	0	19
25	1530.52	2.84	450	1.6	18.9	54.6	664	42.1	0	13.2	0	0.4	3.7	1.1 3	9.5 7(	7	5	0	18
26	1531.32	2.71	446	1.8	15.6	66.5	577	38.9	0.7	11.7	0	3.0	4.6	3.8	7.3 78	3	ę	0	16
27	1532.58	1.46	440	1.1	8.0	77.3	549	24.2	, 0	4.6	0	38.5	7.0	1.2 2	4.5 65	6	ъ	0	19
28	1534.10	1.73	440	1.5	9.9	85.5	574	36.6	0	11.8	2.5	6.0	2.3	0.4 4	0.4 7/	1 2	ŝ	0	21
29	1536.24	0.98	441	0.7	5.0	68.7	509	21.2	0	3.3	0	56.3	4.6	0.7 1	4.0 66	17	0	0	17
30	1537.20	2.85	448	2.5	20.7	86.2	727	37.4	0	12.0	0	11.2	3.6	2.2 3	3.7 74	5	9	0	15
31	1539.80	7.27	453	2.2	49.4	30.1	680	41.7	0	11.4	0.5	6.0	2.1	4.7 3	3.6 68	8	8	0	16
32	1540.43	4.01	449	2.1	24.7	51.9	615	23.8	0	4.6	27.5	13.5	0.6	9.5 2	0.4 56	0	12	0	32

 Table 1

 Bulk geochemical parameters and XRD results of the samples from the first member of the Qingshankou Formation.

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Fig. 3. (a) Plot of  $T_{max}$  versus hydrogen index. (b) Correlation between  $S_2$  and TOC content. (c) Plot of  $S_1$  and TOC content.

According to the study of conventional sandstone reservoirs (Liu and Eadington, 2003), normalized QGF-E intensity greater than 40 pc indicates that the sandstone succession is an oil reservoir. In this study, the normalized QGF-E intensity of Qing-1 shale is as high as 36014.32 pc, with an average normalized QGF-E intensity of 124151.53 pc, which is significantly higher than the QGF-E intensity of a sandstone reservoir. These might be as a result of a much higher surface area ratio of pores containing hydrocarbon in the shale reservoir to the clastic sands. Given the normalized QGF-E intensity, a separate definition of the effective shale oil layer is required.

Results from the TSF test show that different shale samples and

crude oil samples (4 ppm) have very similar three-dimensional fluorescence fingerprint characteristics (the color standard for the fluorescence intensity of a sample), with good uniformity (Figs. 5 and 6a). The MAX-EX is 258 nm while MAX-EM is distributed between 378 and 383 nm. R<sub>1</sub> is greater than 3, and R<sub>2</sub> is larger than the overall R<sub>1</sub> values. The R<sub>1</sub> parameter has an excellent negative correlation with the geochemical parameter Ts/(Ts + Tm), which can be used to determine the maturity and viscosity characteristics of shale oil (Liu and Eadington, 2005). Generally, R<sub>1</sub> > 3.0 and MAX-EX/MAX-EM is medium-heavy oil at about 250/375 nm. As R<sub>1</sub> is at 2.0–3.0, MAX-EX/MAX-EM is light oil at approximately 360/360 nm and for R<sub>1</sub> < 2.0, MAX-EX/MAX-EM

#### Table 2

Bulk	QGF-E and '	ГSF р	arameters	of the	samples	from	the fir	st mer	nber	of the	Qingshankou	Formation.
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Number	Depth/m	Sample	QGF-E		TSF						TSF Oil saturation/
		quanty/ g	$\lambda_{max}/nm$	Normalized QGF-E- intensity/pc	Normalized TSF- MAX/pc	TSF-MAX/ pc	MAX-EX/ nm	MAX-EM/ nm	R <sub>1</sub> /nm	R <sub>2</sub> /nm	VOID
2	1484.30	0.178	380	198088.6	98882.7	948.5	258	378	4.22	6.3	34.14
3	1488.25	0.152	380	112628.4	86403.2	484.5	258	378	3.9	5.6	20.00
5	1492.50	0.133	378	110259.8	87990.7	371.5	258	378	4.4	6.6	17.31
7	1497.08	0.176	379	102284.2	100856.7	501.5	258	378	4.5	6.7	17.91
10	1503.01	0.139	380	118653.7	77385.0	453.9	258	378	4.5	6.9	20.43
14	1511.48	0.156	378	92822.8	112114.4	386.9	258	383	4.9	7.5	15.40
18	1518.43	0.171	380	133408.8	78899.7	616.6	258	378	4.1	6.4	22.84
20	1523.30	0.164	381	91900.7	121427.2	418.2	258	378	3.9	6.1	15.90
23	1528.09	0.090	379	145471.5	116563.9	352.1	258	378	4.4	6.5	24.16
24	1529.59	0130	381	132560.3	166397.0	489.6	258	378	5.1	7.8	23.65
29	1536.24	0.131	380	36014.3	30285.0	127.2	258	378	3.5	4.9	5.36
30	1537.20	0.175	379	135836.0	121397.5	679.8	258	378	4.4	6.5	24.68
31	1539.80	0.160	380	204040.7	165635.9	861.3	258	378	4.7	7.4	34.42



Fig. 4. Spectrogram of the shales by QGF-E analysis in the first member of Qingshankou Formation.

is condensate oil at around 250/340 nm (Liu et al., 2014b). Therefore, both the extract from shales and crude oil are thick medium oil with medium maturity.

The plots of standard solutions with different oil content and the corresponding maximum TSF fluorescence intensity show an obviously positive correlation (Fig. 6b), with a coefficient of determination  $R^2$  of 0.99. The oil saturation of the Qing-1 shales calculated from the maximum TSF fluorescence intensity of shale extract ranges from 5.36 vol% to 34.42 vol% with an of average 21.25 vol% (Table 2).

#### 4.4. 2D NMR results

The  $T_1$ - $T_2$  map of sample number 14 shown in Fig. 7 is a good example that demonstrates the distribution of different phase <sup>1</sup>H in shale. The T<sub>1</sub>-T<sub>2</sub> map is divided into four signal intervals based on the previous interpretations of 2D NMR map (Washburn and Birdwell, 2013; Fleury and Romero-Sarmiento, 2016; Khatibi et al., 2019). The upper left of the map (with  $T_1 = 10 \text{ ms}$  as the approximate dividing line) referred to as zone 1, is determined as the signal area of solid OM (or asphaltene). Zone 2 at the upper right area of the T<sub>1</sub>-T<sub>2</sub> map, is soluble OM interpreted as shale oil from the signal overlap of the shale samples before and after Soxhlet extraction. It should be noted that Li et al. (2018) argued that the signal interval of  $T_2 > 1$  ms and  $T_1/T_2 > 10$ represent light crude oil, but the shale contains a large amount of magnetic minerals such as pyrite and siderite. The magnetic properties of these minerals, therefore, reduce the T<sub>2</sub> value in this section of the signal (Rueslåtten et al., 1998). Consequently, it is not possible to only use  $T_2 > 1$  ms as the boundary of the soluble OM oil during the division. Given the clear separation of the two signals on the map and the shorter T<sub>2</sub> time of solid OM (or asphaltenes) compared to soluble OM, it is more reasonable to use the signal separation as the boundary between solid and soluble OM. Zone 3 at the lower left of the map is a hydroxyl-rich compound, but only in principle. For example, a tightly structured kerogen molecule or a macromolecular branch of a heavy oil also has the ion OH- and could contribute to the signal in the region of zone 3. This leads to a certain degree of coincidence of the signals of zones 1 and 3, with no apparent boundaries. The fourth region, zone 4, at the lower right of the map corresponds to the water signal in the nanopores or micro-cracks, to which the adsorbed water on the surface of some other clay minerals also contributes. In addition, as the maturity of OM increases, the kerogen and heavy oil removed from the aliphatic branch led to aromatization and densification which further increases the  $T_1$  relaxation time. As a result, the signal in the fourth region increases with the decrease of signal intensity in zone 1, which represents solid OM (Khatibi et al., 2019). The remaining  $T_1$ - $T_2$  maps of other samples are shown in Fig. 8. All  $T_1$ - $T_2$  maps show the distribution of different fluids is generally uniform.

The oil content is defined as the ratio of the oil volume (soluble OM, zone 2), measured by high-frequency 2D NMR, to the mass of shale samples. The ratio of the volume of solid OM (asphaltene) depicted in zone 1, to the mass of shale sample defines the content of solid OM with the unit  $\mu$ /g. According to the detection results of different phase fluids by high-frequency 2D NMR (Table 3), for the 13 selected samples, the total fluid volume containing <sup>1</sup>H was 257–1265 µl, with an average content of 5.8 µl/g and the amounts of hydroxyl-rich compounds contained were 6.2–30.1 µl/g, with an average content of 16.2 µl/g. The water content in nano-pores and fractures was 5.2–26.3 µl/g, with an average content of 16.2 µl/g, while the content of oil was 4.5–6.8 µl/g, with an average content of 5.9 µl/g.

# 5. Discussion

# 5.1. Geochemical characteristics and sedimentary response of continental shale

The OM of the Qing-1 shales mainly originated from hydrogen-rich algae, as evidenced by predominant type I kerogen (Liu et al., 2019). The determined  $T_{\text{max}}$  value indicates that the shale is in the mature stage which corresponds to significant oil generation. According to the



Fig. 5. Spectrograms of the shales by TSF analysis in the first member of Qingshankou Formation.



Fig. 6. (a) Spectrograms of the crude oil by TSF analysis. (b) Plot of different oil content and TSF maximum intensity.



**Fig. 7.** Distribution of different phase <sup>1</sup>H in shale from Qingshankou Formation. The left side of each map is the  $T_1$  relaxation time, the upper part is the  $T_2$  relaxation time, the blue line is the measured curve, and the red line is the cumulative curve. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

plots of  $S_1+S_2$  and TOC contents (Peters, 1986, Fig. 9a), for most samples studied, the TOC content > 1.0 wt% and  $S_1+S_2$  > 5 mg HC/g with a maximum of 56.52 mg HC/g. These values and accompanying properties signify the good hydrocarbon generation potential of the continental shale, indicating an excellent base for oil production.

The sedimentary environment largely controls OM enrichment. In comparison to marine shale, the continental shale may be more sensitive to water depth, climate and provenance supply. Under other conditions, the OM abundance of continental shale is negatively correlated with rock granularity (Liu et al., 2019). In the Cretaceous period, the Songliao Basin was under warm and humid paleoclimate with significant amounts of phytoplankton both included in plankton and algae occurring along with abundant OM (Bechtel et al., 2012). During the sedimentary cycle of the Qing-1 member, the depositional environment of the studied area was dominated by semi-deep to deep lakes. The resultant quiet, anoxic environment was a necessary condition for the preservation of sufficient OM supply. Given the background of insufficient supply of terrigenous felsic clastics, the stable hydrodynamic environment and the decrease in deposition rate caused clay minerals to settle to the bottom of the lake, resulting in the gradual increase of shale clay mineral content in the lake center far from the influence of provenance. The clay mineral particles have a large specific surface area allowing easy adsorption of the OM on the surface of the clay mineral particles (Liu et al., 2018), followed by deposition and preservation. There is a modest correlation between clay mineral content and OM abundance in the Qing-1 shale (Fig. 9b) in cases where clay mineral content less is than 35 wt% (Liu et al., 2019). It indicates a slow sedimentary rate and suspension within a standing water column, in which the OM is absorbed on the clay mineral deposits and preserved together which verifies the difference of the deposition process from marine OM. Furthermore, clay content stops increasing with TOC content when the value reaches 35 wt%. It indicates a stratified and saline water column with the lack of inorganic dilution. The combined function of reducing conditions and more sapropelic organic matter are the main reasons for the increase in OM content (Dong et al., 2015). Many of the shale samples have clay mineral content lying between

25 wt% and 40 wt%, less than the average 50 wt% of the Qing-1 member. Furthermore, for clay mineral content more than 25 wt%, the TOC content reaches about 2 wt%, which is also considered as the lower limit of OM abundance for continental shale oil enrichment and high yield by most scholars (Liu et al., 2019). Therefore, the content of clay minerals in the continental shale formation probably could indicate the abundance of OM and the hydrocarbon generation potential of shale. In addition, the rare biological disturbance traces in the shale samples and the existence of a large amount of pyrite and siderite also indicates that the sedimentary environment of the Qing-1 member is dominated by anoxic reduction. This is a favorable condition for the deposition and preservation of OM in the target layer of the study area.

#### 5.2. Shale oil evaluation parameters

The Rock-Eval  $S_1$  is a parameter that reliably characterizes the content of shale oil. There is a strong linear correlation between nuclear magnetic oil content and  $S_1$  (R<sup>2</sup> = 0.86), which verifies that the signal zone 2 depicted by the 2D NMR measurement represents oil within shales (Fig. 10a). The amount of solid OM (or asphaltenes) is also positively correlated with the TOC content in the shale reservoir  $(R^2 = 0.89)$ , indicating that evaluating hydrocarbon generation potential of shale reservoirs via 2D NMR map is feasible (Fig. 10b). The horizontal intercept value is not zero, suggesting some original soluble OM within shales affects the value of TOC content. Compared to rock pyrolysis, high-frequency 2D NMR does not destroy or heat shale samples, which to a certain degree, prevents the loss of light components. High-frequency 2D NMR provides a simple, efficient and nondestructive method for detecting the hydrocarbon generation potential and shale oil content of the shale samples. There is a correlation between normalized QGF-E intensity and pyrolysis  $S_1$  ( $R^2 = 0.59$ ; Fig. 10c), and between oil content and normalized QGF-E intensity  $(R^2 = 0.69; Fig. 10d)$ . This trend shows that hydrocarbons attached to the surface of shale mineral particles in an adsorbed state can also be measured by NMR, further validating the advantages of NMR in detecting original shale fluids.



Fig. 8. The remaining  $T_1$ - $T_2$  NMR maps of the shale in the first member of Qingshankou Formation.

The composition and physical properties of the crude oil were derived from the  $\lambda_{max}$  value and the fluorescence spectrum, while the crude oil composition and maturity information were obtained from  $R_1$  and MAX-EX/MAX-EM. Thus, the combination of high-frequency 2D

NMR and QGF provided a rapid, efficient and convenient method for nondestructive analysis of shale oil content and geochemical characteristics in shale reservoirs. This remedies the shortage of the traditional parameters such as  $S_1$ , chloroform asphalt "A" and OSI, from

Table	3
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	Bulk fluid	l contents of	different	phases are	divided b	y NMR	of the sam	ples from	the first	member of	the Qin	gshankou	Formation
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No.	Depth/m	Sample quality/g	Content of all $^1\text{H}/\mu\text{l}$	Solid OM/µl/g	Hydroxyls/µl/g	Water/µl/g	Soluble OM/µl/g
2	1484.30	20.02	844	13.0	12.9	9.8	6.4
3	1488.25	17.66	875	1.5	30.1	11.8	6.2
5	1492.50	12.85	657	3.7	23.5	18.7	5.2
7	1497.08	22.76	1161	2.1	17.0	26.3	5.7
10	1503.01	21.07	985	2.4	17.1	21.2	6.1
14	1511.48	18.84	366	2.6	6.2	5.2	5.4
18	1518.43	14.49	720	7.1	17.7	19.1	5.9
20	1523.30	21.24	892	6.9	13.6	15.6	5.9
23	1528.09	16.53	938	9.7	16.8	23.9	6.2
24	1529.59	23.65	1265	5.4	19.8	22.3	6.0
29	1536.24	11.51	257	1.5	9.7	6.6	4.5
30	1537.20	22.72	775	3.6	9.5	14.4	6.7
31	1539.80	19.05	1080	16.7	17.3	15.9	6.8



Fig. 9. (a) Plot of TOC content and  $S_1 + S_2$ . (b) Plot of clay mineral content and TOC content. The shadow shows the range of plots of clay mineral content and TOC content from Liu et al. (2019).



Fig. 10. (a) Plot of NMR oil content and S<sub>1</sub>. (b) Plot of NMR solid organic matter content and TOC content. (c) Plot of normalized QGF-E intensity and S<sub>1</sub>. (d) Plot of normalized QGF-E intensity and NMR oil content.



**Fig. 11.** Depth profiles of bulk parameters by 2D NMR and QGF analyses. NMR OM content = (soluble organic matter volume + solid organic matter (asphaltene) volume)/shale sample quality; NMR light to heavy hydrocarbon ratio = soluble organic matter volume/solid organic matter (asphaltene) volume; NMR oil saturation = soluble organic matter volume/(soluble organic matter volume + water volume); NMR oil content = soluble organic matter volume/shale sample quality. Abbreviation: NMR = nuclear magnetic resonance; QGF = quantitative grain fluorescence; OM = organic matter. Order represents the signal zone number in  $T_1$ - $T_2$  map.

which the composition of crude oil and OM, the API and maturity of crude oil are not adequately determined.

#### 5.3. Evaluation of shale oil enrichment

This study demonstrates an effective means of shale oil enrichment interval evaluation, using high-frequency 2D NMR and QGF experiments, combined with traditional geochemical parameters such as TOC content,  $S_1$  and OSI (Fig. 11). Analyses show that the nuclear magnetic OM content represents the total amount of OM in a unit mass of shale reservoir, including the total volumes of solid OM, asphaltene, and oil. Additionally, the ratio of the nuclear magnetic light to heavy hydrocarbon represents the ratio of oil to solid OM and asphaltene in shale reservoirs, which is similar to OSI, and also shows a similar trend as OSI in the longitudinal profile. The NMR oil content is the volume content of soluble OM in a unit mass of shale reservoir derived from NMR, the oil saturation is the percentage of the sum of oil volume, to the sum of water volume, which may be high as the water content of the shale reservoir is low.

The longitudinal section of the formation along the sampling well shows that TOC content has a nearly similar trend with  $S_1$ . TOC content and  $S_1$  have the same trend attribute as NMR OM content, NMR oil content, normalized QGF-E intensity, TSF oil saturation and OSI, which characterizes the content and properties of shale oil in the shallow part of the sampling well. The well interval of 1530–1535 m reveals the high value of OSI, the ratio of NMR light to heavy hydrocarbon, and the abnormal saturation of NMR oil, due to the lower value of the TOC relative to  $S_1$ . Other parameters, such as TOC content,  $S_1$ , NMR OM content, NMR oil content, normalized QGF-E intensity and TSF oil saturation, display characteristics of low values in this interval relative to the upper and lower sections of the well. The deviation of data between the two groups and thus discrepancies in interpreted characteristics indicates that using the traditional OSI parameter as an isolated criterion for selecting layers in the evaluation of shale oil content, is not a sufficient approach.

In the evaluation of the shale oil enrichment interval, the hydrocarbon generation potential of the shale itself should be considered along with the property and content of the shale oil. As the TOC content is 2.0 wt% and the corresponding  $S_1$  is 1.0 mg HC/g, the shale is interpreted to have the best hydrocarbon generation potential. Under the premise of sealed coring, the shale oil enrichment lower limit indexes in the target layer are NMR OM content greater than  $7.5 \,\mu$ l/g, NMR oil content greater than 6.0  $\mu$ l/g, normalized QGF-E intensity greater than 100000 pc and TSF oil saturation greater than 20 vol%. Four sections of shale oil enrichment layer have been determined: A (1485-1490 m), B (1500-505 m), C (1518-1530 m) and D (1537-1540 m). The brittle minerals (quartz, feldspar, and pyrite) contents are 55.6 wt% - 71.3 wt % (with an average of 62.7 wt%) in section A, 55.5 wt% - 60.5 wt% (with an average of 58.1 wt%) in section B, and significantly higher than that in C and D sections. In section C, the brittle minerals content ranges between 37.0 wt% and 61.8 wt% (with an average of 55.9 wt%) and 38.5 wt% - 55.2 wt% (with an average of 51.2 wt%) in section D, which may be more conducive to fracturing transformation. Section C has the highest clay mineral content of 24.5 wt% - 39.5 wt%, with an average content of 35.4 wt%, while section D has the highest carbonate content of 6.5 wt% - 41.0 wt%, with an average content of 19.6 wt%.

Given the parameter anomaly in the interval 1530–1535 m, it is easy to erroneously identify the interval as the section with the best potential if conventional parameters such as OSI are applied alone. From the results of analyses using 2D NMR and QGF methods promoted in this study, the absolute content of total hydrocarbons in this shale reservoir is not high. However, the high ratio of NMR light to heavy hydrocarbon and the high saturation of NMR oil indicate that the content of light components relative to heavy components in hydrocarbons is obviously higher than that in other succession, resulting in the illusion of abnormally high OSI and good exploration potential. The low TOC content indicates that transported hydrocarbons dominate the OM, and the relative enrichment of light hydrocarbon components may be related to the chromatographic effect of hydrocarbon migration.

## 6. Conclusions

The OM of continental shale in the first member of the Oingshankou Formation in the southern Songliao Basin is dominated by type I kerogen and has high TOC content values. The OM maturity is in the mature stage of hydrocarbon generation, which provides a tangible reference for the enrichment of a large amount of shale oil and has good prospects for exploration. The whole rock mineral composition of the K<sub>2</sub>qn<sup>1</sup> is mainly composed of quartz and clay minerals. It has typical terrigenous mineral composition characteristics and exhibits strong mineral composition heterogeneity longitudinally. The positive correlation between clay minerals and OM content, as well as the common existence of protogenesis pyrite and siderite in the shale, shows that the anoxic semi deep to deep lacustrine sedimentary environment was conducive to the preservation of OM on clay minerals during the sedimentary period in the first member of Qingshankou Formation. For the evaluation of shale oil enrichment in the target layer, results of the 2D NMR map and QGF techniques show that the maturity of shale oil has reached the stage of oil generation. The shale oil is a thick medium oil with poor fluidity as it contains a considerable proportion of adsorbed oil. Four sections of shale oil enrichment can be determined, using the standards of TOC content > 2.0 wt%,  $S_1$  > 1.0 mg HC/g, normalized QGF-E > 100000 pc, NMR OM content > 7.5 µl/g, NMR oil content > 6.0  $\mu$ /g and TSF oil saturation > 20 vol%.

In characterizing the geochemical characteristics of shale and the fluidity of shale oil, high-frequency 2D NMR is a nondestructive and rapid method for the detection of solid organic matter (or asphaltene), oil and water content in fractures or pores in shale. In addition to replacing the traditional rock pyrolysis technology, the combination of 2D NMR with QGF can also obtain the properties and maturity of shale oil and avoid the misjudgment of rich oil sections by large OSI caused by relatively small TOC content. Thus, it can be widely used in the evaluation of shale oil enrichment in other areas.

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