



# Article Gas Desorption Characteristics of the Chang 7 Member Shale in the Triassic Yanchang Formation, Yan'an Area, Ordos Basin

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Abstract: In the Yan'an area of the Ordos Basin, the lithological heterogeneity of Chang 7 Member shale is extremely strong. In addition, sandy laminae is highly developed within the Chang 7 Member shale system. In order to explore the gas generation and migration processes of Chang 7 Member shale, geochemical characteristics of desorption gas are comprehensively compared and analyzed. In this study, rock crushing experiments were carried out to obtain shale samples, and desorption experiments were carried out to obtain shale samples and sandy laminated shale samples. For the crushing gas and desorption gas, the volume contents of different gas components were obtained using gas chromatography experiments. The rock crushing experiments revealed that the average volume percentage of CH<sub>4</sub> in Chang 7 Member shale is 61.93%, the average volume percentage of  $C_2H_6$  and  $C_3H_8$  is 29.53%, and the average volume percentage of other gases is relatively small. The shale gas in Chang 7 Member is wet gas; the gas is kerogen pyrolysis gas. Most of the shale gas hosting in Chang 7 Member shale is adsorbed gas. Porosity, permeability and organic matter content are the main geological factors controlling gas migration and gas hosting. Shale with a higher porosity, good permeability and a low organic matter content is conducive to gas migration. The shale gas in Chang 7 Member shale contains CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>, iC<sub>4</sub>H<sub>10</sub>, nC<sub>4</sub>H<sub>10</sub>, iC<sub>5</sub>H<sub>12</sub>, nC<sub>5</sub>H<sub>12</sub>, CO<sub>2</sub> and N<sub>2</sub>. N<sub>2</sub> migrates more easily than CH<sub>4</sub>, and CH<sub>4</sub> migrates more easily than CO<sub>2</sub>. For hydrocarbon gases, gas components with small molecular diameters are easier to migrate. The desorption characteristics of shale might provide clues for guiding hydrocarbon exploration in the study area. The sandy laminated shale with a higher gas content may be the "sweet spot" of shale gas targets. In Chang 7 Member, the locations hosting both shale oil and CH<sub>4</sub> may be the most favorable targets for shale oil production.

Keywords: shale gas; gas desorption; Chang 7 member shale; Yanchang formation; Ordos Basin

# 1. Introduction

With the commercial exploitation of marine shale gas in North America, Bakken, Marcellus, Woodford, Eagle Ford and other regions have become the main production areas for shale gas [1–3]. China has also achieved successful exploitation of marine shale gas in the Sichuan Basin, and most of the output is produced from the Lower Silurian Longmaxi Formation [4]. However, no progress has been made in producing lacustrine shale gas in the Ordos Basin.

In the Yan'an area of the Ordos Basin, the Chang 7 Member shale of the Triassic Yanchang Formation was deposited in a typical lacustrine environment [5] (Figure 1). In 2007, Yanchang Petroleum (Group) drilled the first shale gas well to penetrate the Chang 7 Member shale in the Yan'an area. Since then, dozens of wells have been drilled in the Chang 7 Member to obtain shale gas; most of the outputs are less than 2000 m<sup>3</sup>/d. Geologists have been trying to reveal the factors resulting in the failed exploitation of Chang 7 Member



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**Copyright:** © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). shale gas. The current interpretations are as follows: (1) Chang 7 Member shale is in an oil window, and gas generation is limited due to the low thermal maturity [6,7]; (2) shale gas is usually associated with oil and water within Chang 7 Member shale, and the content of free gas is limited due to the complex hosting states [8]; (3) the gas compositions of Chang 7 Member shale gas are complex, and the methane content is low [8,9]; (4) the shale reservoir is characterized by strong heterogeneity, and the poor porosity and permeability are unfavourable for gas seepages [8,9]; (5) the content of clay minerals is high, and the Hydraulic Jet Fracturing is more complicated than expected [10]. Furthermore, geologists have conducted several tests to explore the gas storage spaces, gas content, gas compositions and isotope compositions [11–13]. Although researchers have conducted a large number of studies, the gas generation and migration processes of Chang 7 Member shale are still under-explored. In this study, rock crushing experiments and desorption experiments were carried out in order to explore the geochemical characteristics of the Chang 7 Member shale gas.



Figure 1. Map showing the location and the stratigraphic succession of the study area.

In the early 1930's, Illing established the theory of primary migration and explained the migration of hydrocarbons from low-permeability source rocks to high-permeability reservoirs [14]. Shale gas is both the in situ generated gas and the in situ hosted gas. The generation and migration of gas components occurs within the shale system; as such, the shale system acts as a good research target for exploring primary migration and petroleum system characteristics [15–19]. Gas components dissolved into oil help increase formation energy and reduce oil viscosity, thereby enhancing oil recovery. Thus, this study will act as a reference for selecting shale hydrocarbon exploitation targets by comparing the contents of different gas components.

# 2. Geological Background

The Ordos Basin, with an area of  $3.7 \times 10^5$  km<sup>2</sup>, is the second largest basin in China [20]. The basin is bounded by the Hetao Graben, the Alashan Platform, the Liupanshan Basin, the Fenwei Graben, the Qilian-Qinling collision zone, and the Luliang Uplift (Figure 1) [20,21]. The Ordos Basin contains six tectonic units, including the Yimeng Uplift, the Shanbei Slope, the Weibei Uplift, the Tianhuan Depression, the Western Fold-Thrust Belt, and the Jinxi Flexural Fold Belt.

The Yan'an area, located in the central-southern part of the Ordos Basin, belongs to the Shanbei Slope (Figure 1). In the Yan'an area, the Triassic Yanchang Formation, with an average thickness of 1100 m, was deposited in a lacustrine environment. The Yanchang Formation contains 10 members (i.e., Chang 10, Chang 9, Chang 8, Chang 7, Chang 6, Chang 5, Chang 4, Chang 3, Chang 2 and Chang 1) [22,23]. The Chang 7 Member, with a thickness of 30 to 100 m and an average thickness of 60 m, contains lacustrine shales with an average thickness of 40 m. Previous studies have performed several geochemistry tests for the Chang 7 Member; these tests indicated its high capability to generate hydrocarbons (Figure 2). The TOC (Total Organic Carbon Content) of the Chang 7 Member is generally higher than 2%, the organic matter is mainly type I and type II, and the thermal evolution stage is generally in the oil window [24–26]. However, the lithological heterogeneity of Chang 7 Member shale is extremely strong, and sandy laminae (mm- to cm-scale) is highly developed within the member (Figure 2). Previous studies also suggested that the sandy laminae are sandy clastic flow, deposited in the deep lake—semi-deep lake facies [27]. The shale with mm- to cm-scale sandy lamina is classified as sandy laminated shale, while the pure shale is classified as shale [20,25].



**Figure 2.** Photos showing the coexistence of oil, gas and water in the Chang 7 Member shale. (**a**) Oil and gas are seeping from the sandy laminated shale, well Q1240, 1671.47–1671.82 m, core photo; (**b**) Gas is seeping from the shale when submerged in water, well W1447, 1954.68 m, core photo; (**c**) Gas is seeping from the shale when submerged in water, well D1325, 1172.72 m, core photo; (**d**) Oil and gas are seeping from the shale, well D214, 1170.46 m, core photos; (**e**) Oil and gas in the shale are showing fluorescence, well D1339, 1152.37 m, core photo; (**f**) Oil and gas in the shale are seeping from fractures, well W1447, 1954.47 m, core photo; (**g**) Oil and gas in the shale are seeping from fractures, well W1447, 1955.11 m, core photo.

#### 3. Sampling and Experiments

In this study, rock crushing experiments were carried out to obtain shale samples, while desorption experiments were carried out to obtain shale samples and sandy laminated shale samples. The gas contents of different gas components were obtained using gas chromatography experiments. Finally, the gas generation and migration processes were determined by comparing the contents of different gas components.

Seventeen samples were collected from the Chang 7 Member in the Yan'an area for testing and analysis. Five shale samples (S1, S2, S3, S4, S5) were collected from well Y2122, and seven shale samples (S6, S7, S8, S9, S10, S11, S12) were collected from well Q1182. The shale samples collected from these wells were used for rock crushing experiments. Three shale samples (S13, S14, S15) and two sandy laminated shale samples (S16, S17), collected from well W1447, were used for gas desorption experiments. In order to obtain the volume content of different gas components, gases from both experiments were tested using gas chromatography. Basic geological testing, including  $W_r$  (sample weight), burial depth,  $\Phi$  (Rock porosity),  $\rho_r$  (Rock density),  $\rho_0$  (Oil density), TOC (Total Organic Carbon Content), S<sub>1</sub> (Free Hydrocarbon Content), S<sub>2</sub> (Pyrolysis Hydrocarbon Content), T<sub>max</sub> (Maximum Pyrolysis Temperature), S<sub>0</sub> (Oil saturation of rock sample), S<sub>w</sub> (Water saturation of rock sample) and S<sub>g</sub> (Gas saturation of rock sample), was conducted during this study. The parameters of G<sub>s</sub> (content of shale gas), G<sub>f</sub> (content of free gas), G<sub>o</sub> (content of shale gas dissolved in oil), G<sub>w</sub> (content of shale gas dissolved in water) and G<sub>a</sub> (content of adsorbed gas) were also estimated.

The procedure of the rock crushing experiment is as follows: (1) place the fresh samples into the grinding tank equipped with grinding balls; (2) seal the grinding tank and fill it with helium; (3) start the centrifugal device to run the grinding ball at high speed; (4) crush the sample for at least three hours; (5) collect the crushing gas from the grinding tank; (6) measure the volume of the gas; (7) obtain the volume percentage of different gas components using gas chromatography experiments.

The procedure of the gas desorption experiment is as follows: (1) place the fresh samples into the desorption tank; (2) seal the desorption tank and fill it with helium; (3) set the heating rate at  $1 \degree C/min$ ; (4) when the temperature reaches  $30 \degree C$ , measure the volume of desorption gas when the desorption time reaches 12 h and 24 h; (5) obtain the volume percentage of different gas components using gas chromatography experiments when the desorption time reaches 12 h and 24 h; (5) obtain the volume percentage of 12 h and 24 h; (6) when the temperature reaches  $50 \degree C$ ,  $60 \degree C$ ,  $75 \degree C$ ,  $85 \degree C$  and  $95 \degree C$ , maintain the desorption for 24 h and measure the volumes of desorption gas; (7) obtain the volume percentage of different gas components using gas chromatography experiments using gas chromatography experiments.

For the gas chromatography experiments, an Agilent 7890A gas chromatograph (Agilent technologies, Santa Clara, CA, USA) was selected to obtain the volume percentage of the different gas components. The experimental settings of the gas chromatograph are as follows: a MS molecular sieve with a diameter of 3 mm and a length of 2.4 m; a GDX-502 chromatographic column with a diameter of 3 mm and a length of 4 m; the injection pressure of the chromatographic column is maintained at 200 KP. The temperature of the chromatographic column is set to rise from 30 °C to 160 °C, at a heating rate of 70 °C/min. The volume of injected gas is 1 mL; the carrier gas during the experiment is helium; the gas injection temperature in the experiment is maintained at 120 °C; the different gas components are separated by being passed through the capillary column.

The procedures for testing basic geological parameters, including TOC,  $S_1$ ,  $S_2$ ,  $T_{max}$ ,  $S_0$ ,  $S_w$  and  $S_g$ , were described in the previously published papers [20,25].

#### 4. Experimental Results

The gases obtained from both the crushing and desorption experiments in this study contained nine components:  $CH_4$  or  $C_1$  (methane),  $C_2H_6$  or  $C_2$  (ethane),  $C_3H_8$  or  $C_3$  (propane),  $iC_4H_{10}$  or  $iC_4$  (isobutane),  $nC_4H_{10}$  or  $nC_4$  (n-butane),  $iC_5H_{12}$  or  $iC_5$  (isopentane),  $nC_5H_{12}$  or  $nC_5$  (n-pentane),  $CO_2$  (carbon dioxide) and  $N_2$  (nitrogen). The volume

	Rurial Donth				Vol	ume Percer	tage (%)							
Samples	(m)	C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	iC <sub>4</sub>	nC <sub>4</sub>	iC <sub>5</sub>	nC <sub>5</sub>	CO <sub>2</sub>	N <sub>2</sub>				
S1	1717.32	60.33	18.17	13.63	1.31	3.54	0.59	0.64	0.44	0.46				
S2	1720.03	69.23	16.17	10.63	0.62	0.00	0.00	0.00	0.00	0.00				
S3	1761.55	57.89	15.25	14.08	1.33	4.44	0.72	1.00	1.72	0.00				
S4	1763.48	79.47	13.68	5.19	0.34	0.31	0.00	0.00	1.04	0.00				
S5	1765.04	57.88	20.73	12.99	1.05	2.07	0.22	0.15	0.71	4.19				
S6	1423.97	65.30	17.00	10.52	0.89	2.11	0.27	0.20	0.46	3.26				
S7	1424.54	62.33	16.97	13.19	1.22	2.03	0.24	0.22	1.47	2.33				
S8	1427.35	59.22	18.54	13.62	1.17	2.10	0.27	0.28	0.94	3.86				
S9	1429.07	56.96	18.33	12.08	1.09	1.86	0.20	0.15	1.16	8.18				
S10	1431.64	51.86	18.44	12.81	1.17	2.46	0.34	0.30	1.29	11.34				
S11	1432.23	64.60	18.28	12.40	1.12	1.90	0.24	0.20	1.26	0.00				
S12	1434.81	58.14	15.82	15.81	1.87	4.27	0.57	0.47	2.72	0.33				

percentages of different gas components derived from the crushing experiments are shown in Table 1.

 Table 1. The volume percentage of different gas components for gas from crushing experiments.

The volume percentage of different gas components varies greatly in the crushing gas. The volume percentage of C<sub>1</sub> in the crushing gas ranges from 51% to 79%, with an average value of 61.93%; the volume percentage of C<sub>2</sub> and C<sub>3</sub> ranges from 18% to 35%, with an average value of 29.53%; the volume percentage of other gases is relatively small. Of the samples studied, 50% have a volume percentage of C<sub>1</sub> less than 60%; 83% of the studied samples have a volume percentage of heavy gas (C<sub>2</sub> + C<sub>3</sub> + iC<sub>4</sub> + nC<sub>4</sub> + iC<sub>5</sub> + nC<sub>5</sub>) larger than 60% (Figure 3). Generally, natural gas with a volume percentage of C<sub>1</sub> higher than 95% is defined as dry gas; lower than 95% is defined as wet gas.



**Figure 3.** Variation of gas dryness and gas quantity during desorption. (**a**) Variation of gas dryness during desorption; (**b**) Volume percentage of desorbed gas during desorption.

The five samples collected from well Q1182 are three shale samples (S13, S14, S15) and two sandy laminated shale samples (S16, S17). The shale samples had a TOC of >2%, with an average value of 3.12%; the sandy laminated shale samples had a TOC of <2%, with an average value of 1.21% (Table 2). The shale samples had higher values of S<sub>1</sub> + S<sub>2</sub>, with an average value of 4.15%; the sandy laminated shale samples had lower values of S<sub>1</sub> + S<sub>2</sub>, with an average value of 1.59% (Table 2). The shale samples had lower values of  $\Phi$ , with an average value of 6.03%; the sandy laminated shale samples had higher values of  $\Phi$ , with an average value of 7.85% (Table 2). Both the shale samples and the sandy laminated shale samples had medium T<sub>max</sub> values, indicating an oil window maturation. Thus, shale and sandy laminated shale in the study area are excellent source rocks for hydrocarbon generation.

						1											
Samples	Sample Weight (g)	Burial Depth (m)	TOC (%)	S <sub>1</sub> (mg/g)	S <sub>2</sub> (mg/g)	Tmax (°C)	Ф (%)	Pr (g/cm <sup>3</sup> )	ρ <sub>0</sub> (g/cm <sup>3</sup> )	So (%)	S <sub>w</sub> (%)	Sg (%)	Gs (m <sup>3</sup> /t)	G <sub>f</sub> (m <sup>3</sup> /t)	G <sub>o</sub> (m <sup>3</sup> /t)	G <sub>w</sub> (m³/t)	Ga (m <sup>3</sup> /t)
S13	856	1953.77	2.06	1.63	1.48	449	6.3	2.43	0.85	7.40	70	22.60	0.880	0.233	0.188	0.022	0.436
S14	938	1954.25	4.73	2.57	7.24	458	6.1	2.37	0.85	11.75	41	47.25	1.104	0.485	0.296	0.013	0.311
S15	1007	1954.82	2.57	1.12	3.73	452	5.7	2.46	0.85	5.69	39	55.31	1.288	0.511	0.129	0.011	0.637
S16	822	1955.02	0.84	1.28	1.55	447	7.3	2.5	0.85	5.16	47	47.84	1.109	0.557	0.148	0.016	0.389
S17	773	1955.27	1.58	0.85	1.62	451	8.4	2.44	0.85	2.90	51	46.10	1.110	0.632	0.098	0.021	0.359

Table 2. Geochemical parameters of studied samples.

Two shale samples and two sandy laminated shale samples were selected for the gas desorption experiments. In the lower temperature stage of desorption (with a desorption temperature below 50 °C), a large quantity of shale gas was desorbed out of the shale samples and sandy laminated shale samples. In the higher temperature stage of desorption (with desorption temperature above 60 °C), a small quantity of shale gas was desorbed out of the shale samples and sandy laminated shale samples (Table 3) (Figure 3). Thus, most of the shale gas was desorbed from the shale during the lower temperature stage, during which the desorption rate was relatively high. During the desorption, the volume percentage of heavy gas increased as the desorption temperature increased, and the gas dryness ( $C_1/C_{1-5}$ ) of the desorbed gas decreased as the desorption temperature increased (Figure 3a).

Table 3. Volume percentage variations of gas components from desorption.

C 1	Temperature	Time	Volume of	C <sub>1</sub> /C <sub>1-5</sub>	Volume Percentage (%)								
Samples	(°C)	(H)	Desorped Gas (L)	(%)	C1	C <sub>2</sub>	C <sub>3</sub>	iC4	nC <sub>4</sub>	iC <sub>5</sub>	nC <sub>5</sub>	CO <sub>2</sub>	$N_2$
	30	12	0.098	76.8	70.04	6.33	5.77	2.67	4.16	1.55	0.71	3.14	5.63
	30	12	0.063	67.6	62.03	7.81	10.78	4.48	3.38	0.90	2.26	2.12	6.24
	50	24	0.167	69.4	58.74	10.04	6.24	3.22	3.24	1.42	1.75	5.58	9.77
S13	60	24	0.136	68.0	60.55	10.25	4.47	3.24	4.07	3.27	3.16	6.16	4.83
	75	24	0.183	80.8	72.76	6.16	5.52	0.41	2.04	2.13	0.94	3.72	6.32
	85	24	0.095	71.6	67.28	10.13	8.53	2.84	1.17	1.73	2.27	4.48	1.57
	95	24	0.011	53.5	48.87	18.48	10.56	4.17	5.28	1.81	2.04	6.33	2.46
	30	12	0.475	74.9	68 25	10.67	6.24	2 18	2.24	0.76	0.78	1.45	7 /3
	30	12	0.089	74.9	00.25	10.07	0.24	2.10	2.24	0.70	0.78	1.45	7.45
	50	24	0.228	75.7	71.76	9.02	4.65	3.76	3.36	1.25	0.97	1.87	3.36
S14	60	24	0.114	67.2	62.34	14.27	6.2	3.14	4.13	1.47	1.25	4.65	2.55
	75	24	0.085	53.7	48.56	18.64	8.68	4.86	5.97	1.83	1.95	3.47	6.04
	85	24	0.032	40.9	36.77	24.36	10.83	5.62	6.84	2.61	2.78	7.52	2.67
	95	24	0.013	33.6	30.12	27.38	10.94	7.31	7.76	2.87	3.36	8.14	2.12
	30	12	0.574	70.6	70 10	6 42	4 77	1 00	2.25	1 20	0.64	1.04	0 1 2
	30	12	0.233	79.0	72.10	0.45	4.//	1.96	5.55	1.20	0.64	1.24	0.15
	50	24	0.227	77.8	72.67	6.14	5.09	2.68	3.84	2.17	0.87	0.95	5.59
S15	60	24	0.085	62.9	59.15	12.18	8.54	5.41	5.27	2.34	1.15	1.22	4.74
	75	24	0.093	52.0	49.03	15.87	11.31	9.46	4.82	2.45	1.43	2.37	3.26
	85	24	0.062	41.1	40.17	18.6	14.87	13.7	5.86	2.93	1.66	1.03	1.18
	95	24	0.023	35.3	33.94	20.76	17.28	15.14	5.35	2.42	1.38	2.2	1.53
	30	12	0.452	85.8	85 43	717	3 36	1 24	1 57	0.41	0 34	0.48	0
	30	12	0.086	00.0	00.10	7.17	0.00	1.41	1.07	0.11	0.01	0.10	0
	50	24	0.197	76.1	75.2	11.35	5.58	3.79	2.17	0.5	0.28	1.13	0
S16	60	24	0.084	71.1	70.47	10.73	7.35	3.76	5.82	0.55	0.44	0.88	0
	75	24	0.062	56.7	55.97	17.24	11.88	5.05	7.35	0.67	0.58	1.26	0
	85	24	0.023	34.2	33.57	28.24	17.47	8.51	8.9	0.65	0.69	1.97	0
	95	24	0.008	22.5	22.17	33.84	20.55	9.45	10.33	1.24	0.86	1.56	0
	30	12	0.383	81.0	74.18	5.41	4.37	2.24	3.45	1.13	0.76	1.78	6.68
	30	12	0.041	61.0			0.04		0.10	4.45	0.07		
	50	24	0.238	63.5	58.41	14.84	9.84	2.78	3.84	1.45	0.87	2.44	5.53
S17	60	24	0.105	68.4	62.57	12.85	5.54	4.43	3.27	1.64	1.15	3.67	4.88
	75	24	0.046	53.3	48.47	20.77	9.83	4.75	3.52	1.98	1.54	5.75	3.39
	85	24	0.027	45.6	42.25	23.57	11.2	6.58	5.64	2.07	1.42	4.42	2.85
	95	24	0.018	39.0	35.8	25.33	14.01	6.64	5.75	2.23	1.95	5.84	2.45

At desorption temperatures of 30 °C, 50 °C, 60 °C, 75 °C, 85 °C and 95 °C, the volume of desorbed gas decreased as the desorption time increased. For example, during desorption at 30 °C, the volume of desorbed gas in the first 12 h was much larger than that the volume in the second 12 h (Table 3). The total volume of gas desorbed in the second 12 h was only 10% of that desorbed in the first 12 h for sample S17 (Table 3). From this, it can be inferred that gas desorption becomes more difficult over time at a given desorption temperature. However, the volume of desorbed gas increases if desorption temperature is increased. Taking sample S13 as an example, the volume of desorbed gas in the second 12 h was only 0.063 L (at the desorption temperature of 30 °C), while the volume of desorbed gas reached 0.167 L when the temperature was raised to 50 °C. During the latter stage of desorption, only a small quantity of gas can be desorbed gas was only 0.011 L when the temperature was raised to 95 °C.

At different desorption stages, both the absolute and relative content of gas components vary greatly. More specifically, during the six stages (30 °C, 50 °C, 60 °C, 75 °C, 85 °C and 95 °C) of desorption, both the absolute and relative content of  $C_1$  decreased when the experiment shifted from lower into higher temperature stages (Table 3). The absolute content of  $N_2$  decreased when moving into higher temperature stages, whereas the relative content of  $N_2$  showed an irregular change when entering into a higher temperature stage (Table 3).

## 5. Discussion

#### 5.1. Origins of Shale Gas

Shale gas includes both the in situ generated gas and the in situ hosted gas. The generation and migration of gas components occurs within the shale system. It is difficult for gas that has migrated over a long distance to accumulate in the shale system. Prinzhofer et al. tried to determine the origins of shale gas; they established an identification chart using Ln  $(C_2/C_3)$  and Ln  $(C_1/C_2)$  parameters [28]. This chart is useful for distinguishing kerogen pyrolysis gas from oil cracking gas. For the oil cracking gas, the relationship between Ln  $(C_2/C_3)$  and Ln  $(C_1/C_2)$  reveals a positive correlation with a large slope. For the kerogen pyrolysis gas, the relationship between Ln  $(C_2/C_3)$  and Ln  $(C_1/C_2)$  reveals a positive correlation with a small slope. The Ln  $(C_2/C_3)$  in the study area is in the range of 0 to 1, while the Ln  $(C_1/C_2)$  is in the range of 1 to 2. The positive correlation between Ln  $(C_2/C_3)$  and Ln  $(C_1/C_2)$  with a small slope indicates the presence of kerogen pyrolysis gas (Figure 4a).



**Figure 4.** Chart showing the origins of shale gas. (a) Relationship between Ln ( $C_2/C_3$ ) and Ln ( $C_1/C_2$ ); (b) Relationship between  $C_2/C_3$  and  $C_2/iC_4$ .

Using  $C_2/C_3$  and  $C_2/iC_4$  parameters, scholars established another identification chart to distinguish kerogen pyrolysis gas from oil cracking gas. For the kerogen pyrolysis gas, the value of  $C_2/C_3$  is less than 2 and the value of  $C_2/iC_4$  is less than 10; the corresponding vitrinite reflectance is less than 1.5%. For the oil cracking gas, the value of  $C_2/C_3$  is larger than 2 and the value of  $C_2/iC_4$  is larger than 10; the corresponding vitrinite reflectance is larger than 2.0% [29]. All the samples in the study area have  $C_2/C_3$  values less than 2, and most of the samples have  $C_2/iC_4$  values larger than 10, indicating a complex process of gas loss (Figure 4b).

Previously studies have shown that the pressure and temperature balance of the shale system is severely damaged during the drilling process, despite the borehole always being filled with drilling-fluid. Thus, some gas components are lost during the drilling process. Field practices also indicated that some oil, gas and water was lost during sampling (Figure 2). It is speculated that the gas lost during drilling and sampling is likely to have caused the value difference of  $C_2/iC_4$ . Thus, the  $C_2/C_3$  values less than 2 and  $C_2/iC_4$  values larger than 10 may indicate the presence of kerogen pyrolysis gas.

#### 5.2. Shale Gas Content

As previously discussed, some shale gas is lost during drilling and sampling. Thus, the quantity of desorbed gas obtained from the desorption experiment cannot represent the total shale gas content. Shale gas content is the sum of the desorbed gas and the lost gas. At present, no effective method for calculating lost shale gas has been established. However, several methods for calculating lost coal-bed methane have been established, and these methods have been applied to calculate lost shale gas in previous studies [22]. Bertard used the diffusion theory to calculate lost coal-bed methane [30]; Kissel proposed the USBM method to calculate lost coal-bed methane [31]; and Yee and Hanson proposed the polynomial curve to estimate lost coal-bed methane [32].

The Chang 7 Member shale in the study area is characterized by high abundance of organic matter and strong gas adsorption capacity; in addition, the shale gas hosted in Chang 7 Member shale is primarily in the adsorbed state [11–13]. Thus, the USBM method was selected to estimate the content of lost shale gas. The procedure for calculating lost shale gas is as follows: (1) establish the horizontal coordinates using coring and sampling time as well as desorption time; (2) establish the vertical coordinates using volume of desorbed gas and volume of lost gas; (3) draw the coring and sampling times; (4) draw the desorption times; (5) fit the curves using coring and sampling times and desorption times; (6) determine the straight line for the former desorption period on the coordinate diagram; (7) extend the straight line to the lower-left coordinates; (8) determine the volumes of lost gas using coordinates corresponding to coring and sampling times [31].

The theoretical calculation shows that the volumes of lost gas vary greatly among the five samples (Figure 5). Sandy laminated shale samples have the largest volumes of lost gas  $(0.8 \text{ m}^3/\text{t})$ . Shale samples have lower volumes of lost gas,  $(0.62 \text{ m}^3/\text{t})$ . The content of Chang 7 shale gas in the study area ranges from  $0.973 \text{ m}^3/\text{t}$  to  $2.022 \text{ m}^3/\text{t}$ , with an average value of  $1.677 \text{ m}^3/\text{t}$ . The average content of lost gas of Chang 7 shale in the study area is  $0.579 \text{ m}^3/\text{t}$ , accounting for less than 45% of total shale gas content.



Figure 5. Chart showing the calculating of volumes of lost shale gas.

# 5.3. Gas Generating Capability

In most cases, organic matter with a higher organic abundance usually has a higher hydrocarbon-generating capability. Therefore, the relationship between TOC values and rock pyrolysis parameters, including  $S_1$ ,  $S_2$ , and  $S_1 + S_2$ , shows a positive correlation [20,23]. In this study, the relationship between TOC and  $S_2$ , as well as  $S_1 + S_2$ , also shows a positive correlation; this is consistent with general geological conditions (Figure 6a). Previous studies have proved that the thermal evolution of the Chang 7 Member shale in the Ordos Basin is in the oil window stage, and that a large proportion of the organic matter has not yet been transformed into hydrocarbon [7–9]. Thus,  $S_2$  values are generally larger than  $S_1$  values in this study, resulting in a similar trend for  $S_1 + S_2$  and  $S_2$ .



**Figure 6.** Scatter plot showing the gas generating abilities of studied samples. (a) Relationship between TOC and rock pyrolysis parameters; (b) Relationship between TOC and gas dryness as well as volume percentage of CH<sub>4</sub>.

However, there is no obvious positive correlation between TOC values and  $S_1$  values for the studied samples. Recent studies have confirmed that a large number of nanoscale micro-pores and micro-fractures have developed within the shale, and that the shale hydrocarbon migration has occurred within the shale system. Instead,  $S_1$  does not represent the in situ generated shale hydrocarbon.  $S_1$  represents the retained shale hydrocarbon after migration. The sandy laminated shale samples (S16 and S17) with the lowest TOC values have the lowest hydrocarbon generating capability; the shale samples with highest TOC values have the highest hydrocarbon generating capability (Figure 6a). The shale gas content in the study area ranges from  $0.97 \text{ m}^3/\text{t}$  to  $2.02 \text{ m}^3/\text{t}$ , with an average value of  $1.67 \text{ m}^3/\text{t}$ , indicating that the gas generating capability of the Chang 7 Member shale in the study area is relatively low. In this study, sandy laminated shale samples (S16 and S17) had higher volume percentage values of CH<sub>4</sub> and thus higher values of gas dryness (Figure 6b). The shale samples (S13, S14 and S15) had lower volume percentage values of CH<sub>4</sub> and thus lower values of gas dryness (Figure 6b). Coefficients related to CH<sub>4</sub> likely to indicate the gas migration process, because CH<sub>4</sub> migrates more easily than other gases. Thus, the higher content of shale gas for the sandy laminated shale samples is caused by gas migration; a part of gas generated from shale can accumulate in sandy laminated shale, though sandy laminated shale has a relatively low gas generating capability. The lower content of shale gas for the shale samples is also caused by gas migration; a part of the gas generated from shale, although shale has a relatively high gas generated from shale can migrate out of shale, although shale has a relatively high gas generating capability (Table 4).

Table 4. Comparison between lost gas and shale gas.

Samples	Coring and Sampling Times (h)	Volumes of Desorbed Gas (L)	Volumes of Lost Gas (L)	Content of Lost Gas (m <sup>3</sup> /t)	Content of Shale Gas (m <sup>3</sup> /t)	The Ratio of Lost Gas to Shale Gas (%)
S13	7.7	0.753	0.08	0.093	0.973	9.60
S14	8.2	1.036	0.58	0.618	1.723	35.89
S15	9.6	1.297	0.46	0.457	1.745	26.18
S16	16.3	0.912	0.75	0.912	2.022	45.13
S17	17.2	0.858	0.63	0.815	1.925	42.34

#### 5.4. Hosting States of Shale Gas

The hosting states of shale gas can be split into three types: adsorbed gas in adsorbed state, dissolved gas in dissolved state and free gas in free state. For shale gas in the United States, the ratio of the adsorbed state to the total states is in the range of 20% to 85%, varying depending on different geological factors, including abundance of organic matter, types of organic matter, thermal evolution and reservoir space [33–35]. The content of free gas can be calculated by using geological parameters, including porosity and gas saturation of shale samples, which is widely used in calculating the content of natural gas (Table 5). The content of dissolved gas can be obtained by using the solubility chart [35] (Table 5). The content of adsorbed gas can be obtained by subtracting the contents of free gas and dissolved gas from the shale gas content (Table 5).

Table 5. Calculations of hosting states of shale gas.

$G_{d} = G_{o} + G_{w}$ $G_{o} = R_{og} \times S_{1}/(1000\rho_{o})$ $G_{w} = \Phi \times S_{w} \times R_{wg}/(1000\rho_{r})$ $G_{o} = \Phi \times S_{w} \times R_{wg}/(1000\rho_{r})$ $G_{o} = G_{o} + G_{w}$ $S_{w} \text{ parameters are interpreted from well logging data.}$ $S_{w} \text{ parameters are interpreted from well logging data.}$ $G_{o} - \text{content of shale gas dissolv}$ $G_{o} - \text{content of shale gas dissolv}$ $S_{o} - \text{oil saturation of rock sampl}$ $S_{o} \text{ parameters are calculated using the following formula:}$ $P_{o} - \text{content of shale gas dissolv}$ $S_{o} - \text{content of shale gas dissolv}$ $S_{o$	s, m <sup>3</sup> /t; solved in oil, m <sup>3</sup> /t; solved in water, m <sup>3</sup> /t; nple, %; it, mg/g;
$S_0$ parameters are calculated using the following formula: $S_1$ —free hydrocarbon content, n $\rho_0$ —oil density, g/cm <sup>3</sup> ; $\rho_r$ —rock density, g/cm <sup>3</sup> ;	nt, mg/g;
$p_r$ -rock density, g/ cm ,	
$S_{o} = 10 \times S_{1} \times \rho_{r} / (\Phi \times \rho_{o})$ $R_{og} - solubility of gas in oil, m^{3}, \Phi - rock porosity, \%;$	m <sup>3</sup> /m <sup>3</sup> ;
$S_{g}$ parameters are calculated using the $R_{wg}$ —solubility of gas in water, following formula:	sample, %; ter, m <sup>3</sup> /m <sup>3</sup> ;
$S_g = 1 - S_o - S_w$ $S_g = - S_o - S_w$ $S_g = - S_o - S_w$ $S_g = - S_g - S_g$ $S_g - S_$	t; imple, %;
$G_{a} \qquad \begin{array}{c} G_{a} = G_{s} - G_{o} - G_{w} - G_{f} \\ G_{s} = W_{r}/(1000 \times G_{desorption}) \end{array} \qquad \begin{array}{c} R_{wg} \text{ and } R_{og} \text{ parameters are obtained} \\ using the using solubility chart, and \\ their values are 1.2 m^{3}/m^{3} \text{ and} \end{array} \qquad \begin{array}{c} G_{a} - \text{content of adsorbed gas, m} \\ W_{r} - \text{weight of rock, g;} \end{array}$	s, m <sup>3</sup> /t; /t;

As previously discussed, some shale gas is lost during drilling and sampling. Thus, there is a hypothesis that the three states of shale gas are lost equally during drilling and sampling when using the method mentioned in this study. The calculation results of five samples show that the hosting states of shale gas in the study area are primarily the adsorbed state and free state. The content of adsorbed gas ranges from  $0.31 \text{ m}^3/\text{t}$  to  $0.64 \text{ m}^3/\text{t}$ , with an average value of  $0.43 \text{ m}^3/\text{t}$ ; the content of dissolved gas ranges from  $0.12 \text{ m}^3/\text{t}$  to  $0.31 \text{ m}^3/\text{t}$ , with an average value of  $0.19 \text{ m}^3/\text{t}$ ; the content of free gas ranges from  $0.23 \text{ m}^3/\text{t}$  to  $0.63 \text{ m}^3/\text{t}$ , with an average value of  $0.48 \text{ m}^3/\text{t}$ ; the content of free gas ranges from  $0.23 \text{ m}^3/\text{t}$  to  $0.63 \text{ m}^3/\text{t}$ , with an average value of  $0.48 \text{ m}^3/\text{t}$  (Figure 7). The average volume percentage of free gas is 37.6%, the average volume percentage of dissolved gas is 20.1%, and the average volume percentage of free gas is 53.6%, the average volume percentage of adsorbed gas is 33.7% for the two sandy laminated shale samples (Figure 7). Thus, the content of adsorbed gas in shale is larger than that of free gas, whereas the content of free gas in sandy laminated shale is larger than that of adsorbed gas.



Figure 7. The hosting states of shale gas in Yanchang Formation shale.

The abundance of organic matter and porosity and permeability are likely to be the influencing factors for the differences in hosting states between shale and sandy laminated shale. Sandy laminated shale generally has a lower abundance of organic matter, with an average TOC of 1.21% across the two measured samples; the shale generally has a larger abundance of organic matter, with an average TOC of 3.12% across the three measured samples. As the abundance of organic matter is the most important factor affecting adsorption, the sandy laminated shale with the lower abundance of organic matter has a lower adsorption capability, leading to a lower content of adsorbed gas. Experimental results from well YCYV1112 in the study area showed that the pore sizes of the sandy laminated shale were in the range of 10 to 50 nm, while the pore sizes of shale were in the range of 5 to 20 (Figure 8) [25]. The sandy laminated shale samples in this study had an average porosity of 7.9%, while the shale samples had an average porosity of 6.0%. Thus, the sandy laminated shale with the larger pore sizes usually had a higher porosity and permeability, leading to a lower content of adsorbed gas.



**Figure 8.** Scatter plot showing the pore widths of samples in YCYV1112 well [25]. (**a**) Pore widths of sandy laminated shale samples; (**b**) Pore widths of shale samples.

# 5.5. Migration Capability of Different Gases

The adsorption of fine-grained sediments (such as mudstone, shale and coal) to gas is a physical adsorbing process; the adsorbing capability is controlled by Van der Waals bonds [36]. Due to the differences of van der Waals force between different molecules, fine particle components have different adsorbing capabilities for different gas components. As a mixture of various gases, the different components of shale gas have different adsorbing capabilities within the shale system, resulting in the desorbing differentiation during desorption. Therefore, an effective way to explore the migration capability of different gases is to use desorbing differentiation during desorption.

Four samples (S14, S15, S16, S17) had similar desorbing patterns during the desorption. During the desorption, the gas dryness of desorbed gas decreased, the volume percentage of heavy gases increased, the volume percentage of  $CO_2$  increased and the volume percentage of  $N_2$  decreased (Figure 9). The above observation indicates that  $CO_2$  and heavy gases have migration capabilities lower than  $CH_4$  and  $N_2$ , and they are easier to migrate out of shale. A large portion of  $CH_4$  and  $N_2$  can migrate out of shale at low temperatures, while a large portion of  $CO_2$  and heavy gases can only migrate out of shale at high temperatures. The ratio of  $N_2$  decreases rapidly while the ratio of  $CH_4$  decreases slowly during the desorption; this probably indicates that  $N_2$  has a relatively higher migration capability than  $CH_4$ . Furthermore, some samples have higher ratios of desorbed  $CO_2$  during the latter desorption period; this probably indicates that heavy gases has a higher migration capability than  $CO_2$  (Figure 9).

The relative ratios of the different components of heavy gas can be used to estimate migration capabilities [29]. The relationship between  $C_1/C_2$  and  $C_2/C_3$  and the relationship between  $C_2/C_3$  and  $C_3/nC_4$  have been shown to be effective parameters for estimating the migration capabilities of heavy gases [29]. In this study, both the shale samples and sandy laminated shale samples showed similar desorbing patterns. The  $C_1/C_2$  values and  $C_2/C_3$  values showed a linear correlation on the scatter plot; the  $C_2/C_3$  values and  $C_3/nC_4$  values also showed a linear correlation on the scatter plot (Figure 10). The above pattern strongly indicates that heavy gases with larger molecular diameters have the lowest migration capabilities. Thus, the migration capabilities of heavy gases conform to the following sequence:  $C_2 > C_3 > nC_4$ .



**Figure 9.** Scatter plot showing the migration ability of different gases. (a) Relationship between gas dryness and volume percentage of  $CH_4$ ; (b) Relationship between gas dryness and volume percentage of heavy gases; (c) Relationship between gas dryness and volume percentage of CO<sub>2</sub>; (d) Relationship between gas dryness and volume percentage of N<sub>2</sub>.



**Figure 10.** Scatter plot showing the migration ability of heavy gases. (a) Relationship between  $C_1/C_2$  and  $C_2/C_3$ ; (b) Relationship between  $C_2/C_3$  and  $C_3/nC_4$ .

The desorption characteristics of shale might provide clues to guide hydrocarbon exploration in the study area. As sandy laminated shale samples commonly have the highest content of free gas, favored for production, the sandy laminated shale with highest gas content could be the "sweet spot" for shale gas targeting.

Gas dissolved in oil could help increase formation energy and reduce oil viscosity, thereby enhancing oil recovery. Xue proved that, with a temperature below 75 °C and a pressure less than 60 MPa,  $CH_4$  can be dissolved in oil more easily than  $CO_2$ , and that  $CO_2$  can be dissolved in oil more easily than  $N_2$ . The Triassic Yanchang Formation is

characterized by low formation pressure and low formation temperature (less than 50 MPa and 60 °C) [37]. Thus, it can be inferred that the locations hosting both shale oil and CH<sub>4</sub> may be the most favorable targets for shale oil production.

## 6. Conclusions

Gas in the Chang 7 Member shale is wet gas, and the Chang 7 Member shale gas is kerogen pyrolysis gas.

Most of the shale gas in the Chang 7 Member shale is adsorbed gas. Porosity, permeability and organic matter content are the primary geological factors controlling shale gas migration and hosting state.

Sandy laminated shale with the highest gas content may be the "sweet spot" of shale gas targets. In the Chang 7 Member, the locations hosting both shale oil and  $CH_4$  may be the most favorable targets for shale oil production.

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