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Controls on Pore Structures and Permeability of Tight Gas Reservoirs in the Xujiaweizi Rift, Northern Songliao Basin

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MDPI

Abstract: As significant components of tight gas reservoirs, clay minerals with ultrafine dimensions play a crucial role in controlling pore structures and permeability. XRD (X-ray diffraction), SEM (scanning electron microscopy), N₂GA (nitrogen gas adsorption), and RMIP (rate-controlled mercury injection porosimetry) experiments were executed to uncover the effects of clay minerals on pore structures and the permeability of tight gas reservoirs, taking tight rock samples collected from the Lower Cretaceous Dengloukou and Shahezi Formations in the Xujiaweizi Rift of the northern Songliao Basin as an example. The results show that the pore space of tight gas reservoirs primarily comprises intragranular-dominant pore networks and intergranular-dominant pore networks according to fractal theory and mercury intrusion features. The former is interpreted as a conventional pore-throat structure where large pores are connected by wide throats, mainly consisting of intergranular pores and dissolution pores, and the latter corresponds to a tree-like pore structure in which the narrower throats are connected to the upper-level wider throats like tree branches, primarily constituting intercrystalline pores within clay minerals. Intragranular-dominant pore networks contribute more to total pore space, with a proportion of 57.79%–90.56%, averaging 72.55%. However, intergranular-dominant pores make more contribution to permeability of tight gas reservoirs, with a percentage of 62.73%–93.40%. The intragranular-dominant pore networks gradually evolve from intergranular-dominant pore networks as rising clay mineral content, especially authigenic chlorite, and this process has limited effect on the total pore space but can evidently lower permeability. The specific surface area (SSA) of tight gas reservoirs is primarily derived from clay minerals, in the order of I/S (mixed-layer illite/smectite) > chlorite > illite > framework minerals. The impact of clay minerals on pore structures of tight gas reservoirs is correlated to their types, owing to different dispersed models and morphologies, and chlorite has more strict control on the reduction of throat radius of tight rocks.

Keywords: clay minerals; pore structures; permeability; tight gas reservoirs; Xujiaweizi Rift; Northern Songliao Basin

1. Introduction

Enormous success in the exploration and exploitation of tight sandstone gas, a kind of unconventional clean natural gas resources, has been achieved worldwide [1–4]. Works on pore systems in tight gas sandstone reservoirs, including pore types, pore-throat sizes and distributions, etc., have drawn great attention because they have significant effects on the storage and flow capacities of tight rocks [5–10]. Many fluid invasion and radiation methods have been applied to disclose pore systems of tight gas sandstones [8,11,12]. The fluid invasion methods primarily include mercury injection porosimetry (MIP), low field nuclear magnetic resonance (NMR), low-pressure gas adsorption (N₂ and CO₂), etc., and the radiation methods principally employ scanning electron microscopy (SEM), small/ultrasmall angle neutron scattering (SANS/USANS), X-ray computer tomography (XCT), etc. Owing to the broad scope of pore-throat dimensions, various techniques need to be integrated to uncover the complete pore systems of tight gas sandstones [6,13].

The pore systems and seepage capacity of tight gas sandstones are simultaneously controlled by multiple factors, such as primary sedimentary environment (particle size, sorting, rounding, mineral compositions, etc.), diagenesis (mechanical compaction, cementation, recrystallization, dissolution, etc.), and regional tectonic movement (fractures) [14-16]. As an important matrix component of tight gas sandstones, clay minerals are generally characterized by ultrafine particle sizes, special morphological structure, and physicochemical properties [17,18]. Currently, research about clay minerals in unconventional reservoirs primarily focuses on their evolution, methane (CH₄) adsorption characteristic, specific surface area, and pore-throat size distributions [18–20]. For instance, Neasham [21] proposed that clay minerals are generally distributed in a pore-throat space in the form of discrete particles, intergrown crystal linings on pore inner surface, or crystals bridging across pores, and they often block throats, resulting in the destruction of pore structure and poor permeability [22]. Ji et al. [23] argued that smectite has the strongest adsorption capacity for CH₄, and physical adsorption is dominant in this process. Chen et al. [17] reported that pores contained in clay minerals are multiscaled from micron to nanosize, which are further classified into interlayer pores, intergranular pores, pores and fractures related to organic matter, pores and fractures related to other types of minerals, dissolution pores, and microfractures. Cao et al. [24] and Yang et al. [25] declared that the total content of clay minerals correlates with pore structure parameters derived from nitrogen gas adsorption (N₂GA) and MIP, such as specific surface area, median pore-throat radius, and maximum pore-throat radius. Ola et al. [18] described in detail the evolution of clay minerals during burial process, especially the conversion of smectite to illite, and they further discussed the relationships between clay mineral diagenesis, shown as I/S ordering, and thermal maturity indicators. However, clay minerals in tight gas sandstones usually contain many types, including kaolinite, illite, chlorite, smectite, etc., and their particle sizes, crystal morphologies, and petrophysical properties show tremendous differences. Therefore, various types of clay minerals possess diverse influence degrees on the pore systems and permeability of tight gas sandstones. More importantly, the quantitative characterization of the impacts of clay minerals on pore structure, porosity, and permeability is still weak at present, and this is the main concern of this work.

In this study, nine tight rock samples with different clay mineral content and permeability are selected from the Lower Cretaceous Shahezi and Denglouku Formations in the Xujiaweizi Rift, Northern Songliao Basin, to carry out XRD, SEM, N₂GA, and rate-controlled mercury injection porosimetry (RMIP) analyses. The objectives of this study are (1) to briefly characterize pore structures and introduce clay mineral morphologies of tight gas reservoirs; (2) to quantitatively evaluate different types of pore networks and their contributions to pore space and permeability; and (3) to discuss the controls of clay minerals on pore structures and permeability of tight gas reservoirs.

2. Geological Setting

The Xujiaweizi Rift is known as one of the largest and most significant gas-bearing rifts in the northern Songliao Basin in Northeastern China (Figure 1A) [26,27], occupying an area of approximately

 0.54×10^4 km². Structurally, the Xujiaweizi Rift is located in the Southeast Fault Depression, a first-order tectonic unit of the northern Songliao Basin, which is mainly composed of four third-order tectonic units: the Anda–Shengping uplift belt, the Xudong sag, the Xuxi sag, and the Xudong slope belt (Figure 1B) [28]. The study area appears as a dustpan-like shape extending along near the north–south direction on the whole, characterized by faulting in the west and overlapping in the east, under the comprehensive influence of late compression and strike-slip [26,29].

The studied intervals are the Lower Cretaceous Denglouku and Shahezi Formations, separated by the Yingcheng Formation (Figure 1C), and these two strata have proven to be the most favorable reservoirs for tight gas accumulations over the past decade [30,31]. Specifically, the Shahezi Formation was primarily deposited in fan deltas, braided river deltas, and semideep to deep lacustrine facies environments, forming interbedded thick dark mudstone/coal and coarse-grained clastic rocks, such as conglomerate, sandy conglomerate, and gritstone (Figure 1C) [32,33]. The reservoir quality of the Shahezi tight gas reservoirs is relatively poor, with a porosity of 0.4%–10.7%, mainly <6.0%, and a permeability of 0.01×10^{-15} to 11.20×10^{-15} m², mainly less than 0.1×10^{-15} m² [27], primarily due to the relatively great burial depth of 3000–4500 m. The Denglouku Formation was deposited during a transition period from a rifting stage to depression stage of the Songliao Basin, corresponding to a sedimentary environment of braided rivers, braided river deltas, and lacustrine facies [34], with interbedded sandstones and thin mudstones (Figure 1C). The thickness of the Denglouku Formation primarily ranges from 500 to 1000 m, with a burial depth of primarily shallower than 3500 m [35].



Figure 1. Diagrams showing (**A**) locations of the Songliao Basin and the study area, (**B**) main tectonic units of the Xujiawei Rift and locations of sampling wells, and (**C**) stratigraphic sequence of the Lower Cretaceous Shahezi, Yingcheng, and Denglouku Formations in Xujiaweizi Rift.

3. Experimental Works

3.1. Sample Collection

Nine tight rock samples, with various clay mineral contents of 2–24 wt.% and a permeability of 0.0352×10^{-15} to 2.35×10^{-15} m² (Table 1), were assembled from the Lower Cretaceous Dengloukou and Shahezi Formations in the northern Songliao Basin. As tight rocks with relatively lower porosity and relatively higher clay mineral content are usually hard to serve as high-quality natural gas reservoirs [31], the porosities and clay mineral contents of the studied samples are primarily greater than 6.0% and lower than 25 wt.% (Table 1), respectively. All of the nine regular core plugs, with \approx 2.5 cm in diameter and 3–6 cm in length, were drilled from the relatively homogeneous section parallel to the sedimentary stratigraphy, and each sample was adequately cleaned in the solution of ethyl alcohol and chloroform in advance to remove residual bitumen. The complete core plug samples were first employed to measure porosity and permeability, and then, each core plug sample was cut into two parts, with a length of \approx 1 cm and \approx 2–5 cm, respectively. The larger part was first designed for SEM experiments on fresh and polished surfaces, before a 3–5 g powdered sample (60–80 mesh corresponding to particle size of 180–250 μ m) was utilized for the N₂GA analysis in advance. Then, all of the larger part sample was crushed into finer powder to carry out an XRD analysis. The smaller part was directly applied to the RMIP analysis. The specific experimental procedures are shown in the following section.

Sample ID	Formation	Well ID	Depth (m)	Porosity (%)	Permeability (×10 ⁻¹⁵ m ²)	Mineral Compositions Obtained from XRD (wt.%)								
						Clay Minerals	Chlorite	Illite	I/S	%S	Quartz	Feldspar	Siderite	Calcite
#1	Denglouku	W1	2872.48	6.99	0.93	2	0.26	0.40	1.34	15	63	31	4	0
#2	Denglouku	W2	3012.47	10.0	2.35	4	1.16	0.64	2.20	15	45	45	6	0
#3	Denglouku	W2	3029.14	6.3	0.31	4	1.16	0.80	2.04	15	50	38	8	0
#4	Denglouku	W3	3079.47	8.8	0.26	8	2.88	1.44	3.68	15	54	38	0	0
#5	Denglouku	W3	3085.06	6.5	0.22	16	4.48	2.88	8.64	15	46	38	0	0
#6	Shahezi	W4	3938.31	8.7	0.13	6	4.50	0.78	0.72	10	30	64	0	0
#7	Shahezi	W5	4529.42	7.9	0.09	3	2.76	0.24	0.00	0	41	56	0	0
#8	Shahezi	W6	2772.21	8.8	0.05	24	4.08	3.36	16.56	15	54	19	0	3
#9	Shahezi	W7	3414.61	6.1	0.0352	22	5.50	3.08	13.42	20	60	13	0	5

Table 1. Petrophysical properties and mineral compositions of nine tight rock samples in the Xujiaweizi Rift.

Clay minerals = chlorite + illite + I/S; I/S = mixed-layer illite/smectite; %S = proportion of smectite in I/S.

3.2. Experimental Methods

3.2.1. RMIP

RMIP analyses were carried out using an ASPE-730 Automatic Mercury Intrusion Porosimeter (Coretest Systems, Inc., Closter, NJ, USA) at the Exploration and Development Research Institute of Daqing Oilfield Company Ltd. Tight rock samples were first cut into cubes, with a volume of <2.0 mL or a weight of <5.0 g, to avoid excessive experimental time, and then were dried to a constant weight at 105 °C before the RMIP experiment. To keep a quasistatic mercury intrusion, the intrusion rate of mercury was set as an extremely low fixed value of $\approx 5 \times 10^{-5}$ mL/min. The mercury intrusion pressure ranged from ≈ 0.025 MPa to ≈ 6.2 MPa, matching a throat radius range of $\approx 0.12-29.4$ µm based on the Washburn equation that is shown as follows [36]:

$$r = \frac{2\sigma\cos\theta}{P_c} \tag{1}$$

where *r* is the throat radius; P_c is the mercury intrusion pressure; σ is the mercury interfacial tension, with a value of 485 mN/m [5]; and θ is the mercury wetting angle, with a value of 140° [5].

As shown in Figure 2A,B, the most important process that occurs repeatedly in the RMIP experiment is the drop and increase of mercury intrusion pressure. The sudden drop of mercury intrusion pressure, marked as rheon by Yuan and Swanson [37], represents the passage of nonwetting mercury from the narrower throats into the wider pores, and the pore-throat radius can be obtained from the initial pressure at the beginning of rheon process using Equation (1). The process of increasing mercury intrusion pressure can be further divided into two subprocesses, namely subison and rison, according to Yuan and Swanson [37]. The subison process mainly refers to the region of rising mercury intrusion pressure immediately after its sudden drop, and the increased pressure needs to be below the pressure at which the rheon process occurred (Figure 2A,B). Thus, a subison process represents a connected void space with lower capillary pressure, i.e., pore systems. Rison primarily refers to a region of continuously increasing mercury intrusion pressure, when the subison process finished (Figure 2A,B), until the next rheon occurs, and the increasing capillary pressure has never been reached previously. Therefore, rison usually corresponds to the filling of a connected void space with greater capillary pressure, i.e., throat systems. Based on the above process, we can obtain mercury intrusion curves within pores, throats, and total space (pores + throats), respectively, according to the fluctuations of mercury intrusion pressure. Several commonly used parameters, such as the average ratio of pore to throat radius (RPT_a) and mercury intrusion saturation in pores or throats (S_{pore} or S_{throat}) can be calculated using the following equation:

$$\begin{cases} RPT_{a} = \sum_{i=1}^{n} RPT_{i}f_{i} \\ S_{pore} = \frac{V_{pore}}{\varphi V_{sample}}, S_{throat} = \frac{V_{throat}}{\varphi V_{sample}} \\ S_{total} = S_{pore} + S_{throat} \end{cases}$$
(2)

where f_i is the normalized distribution frequency of RPT_i ; V_{pore} and V_{throat} are the mercury volumes intruded into pores and throats, respectively; φ is the porosity of tight rocks; and V_{sample} is the volume of tight rock sample used in the RMIP experiment.



Figure 2. A small piece of raw RMIP data for sample #2 (**A**), mercury intrusion process analysis of RMIP (**B**), and the pore-throat structure models assumed in RMIP (**C**) and PMIP (pressure-controlled mercury intrusion porosimetry) (**D**) methods, respectively.

Compared with the RMIP method, pressure-controlled mercury intrusion porosimetry (PMIP) can only obtain one mercury intrusion curve [5], with a maximum mercury intrusion pressure of up to \approx 400 MPa corresponding to a pore size of \approx 3.7 nm [36]. The testing time used in the PMIP method is usually 2–3 h, evidently shorter than that spent on RMIP analyses (i.e., 1–2 d). In addition, in the RMIP method, porous media are usually assumed to be composed of pores and throats with different diameters (Figure 2C), which is more consistent with the fine pore structure characteristics of tight reservoirs [38]. However, the porous media primarily consist of capillary bundles with various diameters in the PMIP method (Figure 2D), and thus, this method cannot recognize the difference between pore and throat diameters.

3.2.2. N₂GA

 N_2GA analyses were executed using the QUADRASORB-SI Surface Area and Pore Size Analyzer (Quantachrome Instruments Corp., Boynton Beach, FL, USA). The core plug samples were first powdered to 60–80 mesh, with a particle size of 180–250 µm, and then 3–5 g powdered samples were selected to desiccate under a vacuum environment at 110 °C for approximately 12 h to remove the vapor and capillary water ahead of the N_2GA experiments. The static adsorption capacity method was used to measure the amount of adsorbed nitrogen at 77.3 K. The experimental data were interpreted using multipoint BET (Brunauer–Emmett–Teller) and BJH (Barrett–Joyner–Halenda) to obtain specific surface area and pore size distribution, respectively, as comprehensively described by [39].

The BJH model depicts the capillary condensation phenomenon in a cylindrical pore based on the Kelvin equation [40], which shows the relationship between the relative pressure of nitrogen (P/P_0) and Kelvin radius (r_K), as exhibited in the following equation:

$$\ln\left(\frac{P}{P_0}\right) = -\frac{2\sigma V_L}{RTr_K} \tag{3}$$

where P/P_0 is the relative pressure of nitrogen; σ is the surface tension of liquid nitrogen at 8.85 mN/m [40]; V_L is the liquid molar volume of nitrogen at 34.65 mL/mol [40]; r_K is the Kelvin radius; R is the gas constant (8.314 J/mol/K); and T is the absolute temperature (77.3K).

When the specific parameter values used in the N_2GA experiment are substituted into Equation (3), we can obtain the following simplified equation:

$$r_K = -\frac{0.9543}{\ln(P/P_0)} \tag{4}$$

The average thickness of the adsorbed layer was determined by the Harkins–Jura equation for nitrogen:

$$t = 0.1 \times \left[\frac{13.99}{0.034 - \lg(P/P_0)}\right]^{1/2}$$
(5)

where *t* represents the average thickness of adsorbed layer.

Finally, we can obtain the pore size according to the following equation:

$$D_p = 2 \times (r_K + t) \tag{6}$$

where D_p represents the pore size.

3.2.3. XRD, SEM, Porosity, and Permeability

A Bruker D8 DISCOVER Advanced X-ray Diffractometer (Bruker Nano Inc., Madison, WI, USA) was used to examine the mineral components of tight rock samples, according to the Petroleum and Gas Industry Standard of China: SY/T 5163-2010. The determination of various mineral contents is based on their different X-ray diffraction peak intensity. SEM tests were measured using a TESCAN-MIRA-3XMU Scanning Electron Microscope (TESCAN, Brno, Czech Republic) to directly view the geometric shape of pores and clay minerals. Helium-derived porosity and nitrogen-derived permeability were measured on the core samples by the CoreLab CMS-300 automatic analyzer (Core Laboratories N.V., Houston, TX, USA) at a confining pressure of around 30 MPa, in order to simulate the actual formation conditions as much as possible, according to the SY/T 6385-2016 standard. The core samples were dried in a vacuum oven at 80 °C for approximately 8 h based on SY/T 5336-2006 in order to generate a minimum damage to tight rock samples and to ensure the accuracy of permeability measurement.

4. Results

4.1. Mineralogical and Petrophysical Properties

Porosity, permeability, and mineral components of nine tight rock samples are listed in Table 1. The results display that tight gas rock samples are primarily composed of quartz, feldspar, and clay minerals, and a small amount of siderite and calcite was also found. Quartz and feldspar are the predominant constituents (Table 1), with contents of 30–63 wt.% and 13–64 wt.%, respectively. The content of clay minerals is between 2 wt.% and 24 wt.% (Table 1), and further analyses show that clay minerals mainly contain I/S, chlorite, and illite, corresponding to contents of 0–16.56 wt.%, 0.26–5.5 wt.%, and 0.24–3.36 wt.%, respectively. Due to the great burial depth of the studied samples, the proportion of smectite in I/S is mainly \approx 15% (Table 1), which is in an evolution process from R1 I/S (35% smectite) to R3 I/S (10% smectite), corresponding to a temperature of 170–180 °C [41,42]. Almost no kaolinite was detected in these samples, which may be attributed to the chemical reaction between kaolinite and K-feldspar at a relatively high formation temperature of >100 °C to form illite and aqueous silica [32,43,44], and the latter may precipitate to generate authigenic quartz aggregates or quartz overgrowth, when the formation conditions change. In the study area, the geothermal gradient is \approx 4.4 °C/100 m based on Zhou et al. [45], and the average surface temperature is determined as \approx 5 °C. Thus, the formation temperature obviously exceeds 100 °C when the burial depth of these selected

samples is mainly >3000 m (Table 1). Noticeably, the average clay mineral content of the Denglouku Formation is generally lower than that of the Shahezi Formation, which is probably related to their different sedimentary environments.

The single crystal of illite in studied samples is present as ribbon or featheriness with a relatively regular arrangement (Figure 3A,B), generally between 0.15 and 0.5 μ m, whereas the shape of their aggregates is mostly lamellar or fibrous being attached to pore walls, extending far into or completely across pores. In addition, the illite often coexists with feldspar, as a result of chemical reaction between feldspar and organic acid fluids [46]. The single crystal of chlorite is mainly needle-shaped with a dimension from 2 to 3 μ m, while their aggregates appear as pompon-, flake-, or rose-like, and wrap the particle surface forming chlorite film (Figure 3C,D). This is favorable for the preservation of storage space in tight reservoirs by inhibiting the overgrowth of quartz [47]. I/S commonly occurs as honeycomb or cotton, primarily distributed in pores with discrete particles (Figure 3E,F).





Under a confining pressure of ≈ 30 MPa, the helium porosities of tight gas rock samples are relatively low, mainly ranging from 6.1% to 10.0%, and the nitrogen permeability primarily varies from 0.0352×10^{-15} to 2.35×10^{-15} m². What calls for special attention is that no obvious positive correlation between porosity and permeability exists in studied samples (Table 1), unlike conventional sandstone reservoirs, generally characterized by better positive correlation between porosity and permeability [48]. Furthermore, we also found that the lower content of clay minerals agrees with a higher permeability (Table 1).

4.2. Storage Spaces

The morphology of pores in tight gas reservoirs is extremely complicated due to intense mechanical compaction and cementation. As exhibited in SEM images (Figures 3 and 4), the storage space of tight gas reservoirs in the Xujiaweizi Rift can be divided into three categories: intergranular pores, dissolution pores, and intercrystalline pores. Intergranular pores are primarily distributed between rigid particles (Figures 3E and 4A), such as quartz and feldspar, which have good resistance to compaction. In a polished SEM image, these pores are commonly presented as triangle or polygon with straight and

smooth edges (Figure 4A), and they can be easily formed into residual intergranular pores due to the filling of argillaceous and siliceous cement, such as grain-coating chlorite and authigenic quartz (Figure 4B). Dissolution pores are principally related to unstable components (Figure 4C,D), including feldspar and carbonates, which are susceptible to organic acids. Compared with intergranular pores, these pores have the characteristics of a fairly anomalous pore shape and relatively good connectivity due to the presence of dissolution channels. Intercrystalline pores are mostly found within clay minerals (Figure 3), including I/S, chlorite, and illite. This kind of pores are numerous but are generally below 2 µm in size. These pores can contribute to a certain amount of storage space, but they contribute rather less to the permeability of tight gas reservoirs.



Figure 4. Pore types of tight gas reservoirs in the Xujiaweizi Rift, identified by SEM images. InterC. = intercrystalline; InterG. = intergranular; Diso. = Dissolution. (**A**) Sample #1; (**B**) sample #3; (**C**) sample #6; (**D**) sample #6.

4.3. Pore Structure Derived from N₂GA and RMIP Analyses

As shown in Figure 5, nitrogen adsorption isotherms of nine tight rock samples are attached to Type IV isotherm based on the classification scheme proposed by Brunauer et al. [49], which is a symbol of mesoporous materials (2–50 nm). The hysteresis loops produced by capillary condensation in pores larger than 2 nm are suitable for Type H3 according to IUPAC (International Union of Pure and Applied Chemistry) classification [50], which are usually interpreted to slit-shaped pores given by aggregates of ductile plate-like particles, mainly clay minerals, as exhibited in Figure 6. The above features are consistent with the observations of tight rocks from the Yanchang Formation in the Ordos Basin [19]. The pore volumes and specific surface areas of nine tight rock samples from the N₂GA analyses present a wide range, as listed in Table 2. Sample #8 shows the highest surface area at 3.41 m²/g, while sample #7 shows the lowest at 0.213 m²/g, with a mean of 1.23 m²/g. The values of specific surface area are quite similar with the tight gas siltstone samples studied by Clarkson et al. [11]. Sample #8 corresponds to the largest pore volume at 0.010213 cm³/g, whereas sample #3 has the smallest value of 0.002324 cm³/g.



Figure 5. Nitrogen (N₂) adsorption–desorption isotherms of nine tight rock samples in the Xujiaweizi Rift.



Figure 6. The slit-shaped pores related to the aggregates of plated-like clay minerals.

Table 2. Pore structure properties derived from N₂GA and RMIP experiments for nine tight rock samples in the Xujiaweizi Rift.

Sample ID	N ₂ G	A Experiment	RMIP Experiment								
	SSA, m²/g	Pore Volume, mL/g	$S_{total}, \%$	Spore, %	$S_{throat}, \%$	<i>RPT</i> _a	<i>ra</i> , μm	<i>r</i> _d , μm	$r_m, \mu m$	P_d , MPa	
#1	0.5460	0.002369	65.70	25.44	40.26	86.78	2.179	2.682	1.011	0.274	
#2	0.8351	0.004179	59.96	17.36	42.61	94.00	1.931	2.822	1.693	0.260	
#3	0.4111	0.002324	63.73	9.46	54.27	81.10	1.918	2.913	0.121	0.252	
#4	1.1573	0.005595	65.08	28.13	36.95	199.09	0.854	1.032	0.322	0.712	
#5	1.3059	0.007224	49.77	8.02	41.75	235.40	0.671	0.658	0.276	1.118	
#6	0.7477	0.006175	45.67	8.94	36.73	203.90	1.077	0.913	0.015	0.805	
#7	0.2132	0.002652	54.77	19.11	35.66	296.64	0.560	0.766	0.235	0.959	
#8	3.4067	0.010213	43.11	7.26	35.85	332.32	0.555	0.633	0.016	1.161	
#9	2.4681	0.008955	26.25	1.65	24.60	178.56	0.611	0.307	0.021	2.396	

SSA = specific surface area; S_{total} = total mercury intrusion saturation; S_{pore} = mercury intrusion saturation in pores; S_{throat} = mercury intrusion saturation in throats; RPT_a = ratio of pore to throat radius; r_a = average throat radius; r_d = maximum connected throat radius corresponding to displacement pressure; r_m = mainstream throat radius; P_d = displacement pressure.

The RMIP curves of the nine studied tight sandstones are displayed in Figure 7. At the initial period of mercury intrusion, the shape of total intrusion curves is more consistent with that of throat intrusion curves, and this coincident trend will be more evident with decreasing permeability (Figure 7). The total mercury intrusion saturation derived from the RMIP method ranges from 26.25% to 65.70%, averaging 52.67% (Table 2), and the mercury intrusion saturation in throats mainly ranges from 24.60% to 54.27% (38.74% on average), evidently higher than that in pores corresponding to 1.65%–28.13% (13.93% on average). Owing to the relatively low mercury intrusion pressure (\approx 6.2 MPa), a large proportion of pores below 0.12 µm in radius cannot be well revealed by this method.



Figure 7. RMIP curves of total (pores + throats), pores and throats for the studied tight rock samples in the Xujiaweizi Rift.

As shown in Figure 8, the pore size of tight rocks obtained from N₂GA method mainly ranges from several nm to ≈ 200 nm (red columns). For the RMIP method, all of the tight rock samples exhibit similar pore size distributions primarily ranging from 200 to 600 µm in dimensions (blue columns), and the pore volumes show a sharp decrease with increasing clay mineral content (Figure 8), whereas their throat size distributions witness considerable differences (green columns), mainly between 0.24 and 6 µm (Figure 8). The average *RPT_a* is between 81.10 and 332.32 (Table 2), exhibiting a positive correlation with clay mineral content. Based on Figure 8, we also found that with increasing clay mineral contents and decreasing permeability, the throat distribution curves (black solid lines) are narrower, and the values of throat size drop gradually. In addition, several relevant throat radius parameters, such as r_a (average throat radius), r_d (maximum connected throat radius corresponding to displacement pressure), and r_m (mainstream throat radius), are positively correlated with permeability, as Figure 9 exhibits, which further indicates that the throat radius rather than pore radius controls the flow properties of tight rocks.



Figure 8. Pore size distributions of nine tight rock samples with various contents of clay minerals and permeability analyzed by nitrogen gas adsorption (N_2GA) and RMIP experiments. The number inside the parentheses is the content of clay minerals.



Figure 9. Correlations between permeability and r_a (average throat radius), r_d (maximum connected throat radius corresponding to displacement pressure), r_m (mainstream throat radius) obtained from the RMIP method.

5. Discussions

5.1. Classification of Pore Networks Based on Fractal Theory

Many studies have demonstrated that pore networks of clastic rocks have statistical self-similarity, characterized by their constantness with various scales [51–53]. Pfeifer and Avnir [54] proposed an equation for calculating surface fractal dimension using mercury intrusion data as follows:

$$\log\left(-\frac{dV_r}{dr}\right) \propto (2 - D_s)\log(r) \tag{7}$$

where V_r is the accumulated mercury intrusion volume when the throat radius larger than r, and D_s is defined as the surface fractal dimension. By plotting the dV_r/dr vs. r under double logarithmic coordinates, D_s can be determined through the slope of the fitting line.

The dV_r/dr vs. r obtained from RMIP data shows evident linear relationships (Figure 10A–C), illustrating that the pore-throat networks of studied tight rocks are generally fractal. Noticeably, the dV_r/dr vs. r curves can be divided into two segments at various throat radii for all tight rock samples, and the fractal dimension (D_{s2}) at the low-pressure section is generally greater than that at the high-pressure section (i.e., D_{s1}), which is consistent with studies of Lai and Wang [53]. This phenomenon is possibly attributed to (1) the skin impact related to the rough surface, (2) the presence of microfractures, or (3) the oversimplified assumption of cylindrical pores [53,55]. Evidently, the pore-throat networks corresponding to these two fractal segments cover disparate mercury intrusion features.



Figure 10. Surface fractal structure of throats (**A**–**C**) and mercury intrusion curves of total (pores + throats), pores and throats (**D**–**F**), derived from the RMIP experiment of three typical tight rock samples. (**A**,**D**): Sample #1, 0.93 mD; (**B**,**E**): sample #2, 2.35 mD; (**C**,**F**): sample #4, 0.26 mD.

In the wider throat part, the total mercury intrusion saturation goes up rapidly covering a confined scope of capillary pressure (Figure 10D–F). For example, the mercury intrusion saturation increases by 32.51%, comprising 49.49% of total mercury intrusion saturation, from 13.12% to 45.63%, when the intrusion pressure rises from 0.27 to 0.96 MPa in sample #1 (Figure 10D). Furthermore, the mercury intrusion process in pores is primarily completed at this stage, and the amount of mercury intruded into the pores in this stage accounts for 76% of total amount of mercury intruded into the pores for sample #1. Sakhaee-Pour and Bryant [56] regarded this type of pore-throat networks as conventional intergranular-dominant networks corresponding to large pores with wide throats (Figure 11A). As demonstrated by the polished SEM image in Figure 11C, intergranular-dominant networks mainly contain intergranular pores and dissolution pores with relatively larger dimensions, and slim pores between grains are treated as throats.



Figure 11. Schematic diagrams showing (**A**) conventional pore-throat structures that larger pores are connected by wider throats, and (**B**) tree-like pore structures that the narrower throats are connected to the wider throats like tree branches. (**C**) SEM image of sample #4 exhibiting an intergranular-dominant and intragranular-dominant pore network. P-pore; T-throat.

In the narrower throat part, the total mercury intrusion saturation grows almost exponentially with the capillary pressure at relatively high pressures, displaying nearly a straight line under semilogarithmic coordinates (Figure 10D–F). The intruded mercury in this stage is almost contributed by the mercury intrusion in throats, with nearly no increase of mercury invaded in the pores. For instance, the mercury intrusion saturation of throats makes up 99.28% of the total mercury intrusion in sample #1 at this stage, i.e., there is no longer any significant discrepancy in pores and throats. Intragranular-dominant pore networks were used to depict this region instead of the abovementioned intergranular-dominant networks, and moreover, Sakhaee-Pour and Bryant [56] adopted a tree-like pore network for the intragranular-dominant region. Intragranular-dominant networks mainly consist of throats with different sizes and lengths, and the narrower throats are connected to the wider throats like tree branches (Figure 11B). As shown in the SEM image in Figure 11C, intragranular-dominant networks predominantly correspond to intercrystalline pores within clay minerals.

The proportions of intergranular-dominant pore networks, determined by RMIP analyses using fractal theory, are listed in Table 3. The proportion of intergranular-dominant pore networks of studied tight samples is between 9.44% and 42.21%, with a mean of 27.45%, implying that intragranular-dominant pores contribute more to pore space. The proportion of intragranular-dominant pore networks is relatively high even for samples with a low clay minerals content. For example, the clay mineral contents of sample #1 and #7 are 2 wt.% and 3 wt.%, respectively, however, their intragranular-dominant pore network percentages still exceed 50%, up to 50.79% and 70.1%, respectively. This may be related to the fact that clay minerals are generally distributed in the intergranular and dissolution pores, resulting in a considerable number of pores associated with clay minerals.

Table 3. Lists of the contributions of intergranular-dominant pore networks to total pore space and
permeability and the contributions of various compositions to SSA calculated from Equation (8) for the
studied nine tight rocks.

Sample	r _{ip} , μm	Contribution of InterGdominant Pores to Pore	Contribution of InterGdominant Pores to Permeability, %	Measured SSA, m²/g	Calculated SSA,	Contributions of Various Compositions to SSA, %				
ID		Space, %			m²/g	Illite	Chlorite	I/S	FM	
#1	0.768	42.21	88.14	0.5460	0.2578	9.53	7.48	80.67	2.32	
#2	0.718	33.99	89.63	0.8351	0.4726	8.32	18.19	72.25	1.24	
#3	0.634	35.07	93.40	0.4111	0.4576	10.74	18.79	69.19	1.28	
#4	0.457	33.90	70.21	1.1573	0.8787	10.07	24.29	65.00	0.64	
#5	0.467	21.96	62.73	1.3059	1.8550	9.54	17.90	72.29	0.28	
#6	0.419	21.47	69.71	0.7477	0.4989	9.60	66.85	22.40	1.15	
#7	0.305	29.90	75.19	0.2132	0.2252	6.55	90.83	0.00	2.63	
#8	0.326	19.08	67.91	3.4067	3.0836	6.69	9.81	83.35	0.15	
#9	0.307	9.44	14.45	2.4681	2.6844	7.05	15.19	77.59	0.18	

 r_{ip} = throat radius at inflection point; InterG.-dominant = intergranular-dominant; SSA = specific surface area; I/S = mixed-layer illite/smectite; FM = framework minerals.

The total clay minerals and various types of clay minerals are also correlated to the proportion of intergranular-dominant pore networks, as shown in Figure 12 and as the contents of total clay minerals, chlorite, illite, and I/S increase, the proportions of intergranular-dominant pore networks drop. Previous studies revealed that clay minerals are commonly derived from terrigenous detritus, namely primary clay minerals, and the chemical reaction between fluids and unstable minerals or the transformation between clay minerals, namely authigenic clay minerals [46,57]. Primary clay minerals are principally distributed in intergranular pores during the initial deposition stage, while authigenic clay minerals are dispersed in intergranular pores and dissolution pores during middle diagenesis stage. The increase of primary or authigenic clay mineral contents will obviously promote the evolution of intergranular-dominant pore networks (intergranular or dissolution pores) to intragranular-dominant pore networks (intercrystalline pores). We also found that chlorite is more closely correlated to the proportion of intergranular-dominant pores compared with illite and I/S (Figure 12B–D), illustrating that chlorite may be more effective in promoting the above pore evolution process, and thus may make more contribution to intragranular-dominant porosity. Although the increase of clay mineral content substantially promotes the evolution of intergranular-dominant pore networks to intragranular-dominant pore networks, and also it changes the relative proportions of these two types of pore networks, this does not necessarily result in an evident change in total storage space, due to the fact that there is unclear link between clay mineral content and total porosity (Table 1).



Figure 12. Relationships between contents of total clay mineral (**A**), chlorite (**B**), illite (**C**), I/S (**D**), and proportions of intergranular-dominant pores.

The throat radius at inflection point (r_{ip}), boundary of intergranular-dominant pores and intragranular-dominant pores, ranges from 0.305 to 0.768 µm (Table 3), indicating that intragranulardominant pore networks of different samples correspond to inconsistent throat size distributions due to multiple degrees of diagenesis and different rock compositions [17,58,59]. The values of r_{ip} are negatively correlated with contents of total clay minerals, chlorite, illite, and I/S (Figure 13), and furthermore, chlorite has the relatively stronger control on r_{ip} (Figure 13B), while the correlations between r_{ip} and illite, I/S are fairly poor (Figure 13C,D).This implies that chlorite is more efficient in lowering values of r_{ip} in relative to illite and I/S, due to the fact that chlorite contributes more to intragranular-dominant pore networks, as evidenced by Figure 12.



Figure 13. Throat radius at inflection point (r_{ip}) vs. contents of total clay minerals (**A**), chlorite (**B**), illite (**C**), and I/S (**D**).

5.2. Effect of Clay Minerals on Pore Structure Properties

The positive correlation between total clay minerals and SSA is pretty good, as exhibited in Figure 14A, indicating the strong control of clay minerals on SSA of tight rock samples. Specifically, both illite and I/S contents exhibit fine positive correlations with SSA, with a R^2 of 0.81 and 0.94 (Figure 14C,D), respectively, while there is a relatively poor positive relationship between chlorite and SSA ($R^2 = 0.37$, Figure 14B). In contrast to framework particles, such as quartz, feldspar, and calcite, clay minerals generally have colossal surface area due to their lamellar and plate-like crystal structure and small particles [19,20,60]. Thus, clay minerals are the main contributor to SSA of tight rocks, and the greater the clay mineral content, the greater the SSA. Furthermore, due to the existence of internal surface area, smectite usually corresponds to a total SSA of up to 800 m²/g, whereas the total SSA of illite and chlorite are relatively low at 30 m²/g and 15 m²/g, respectively, as reported by Passey et al. [20]. We can speculate that I/S, which is the intermediate product from smectite to illite [61], should also possess a greater SSA than that of illite and chlorite. Thus, the contribution of various clay minerals to the total SSA is distinct, which well interprets the differences in the correlation coefficients between different types of clay minerals and SSA (Figure 14B–D).



Figure 14. Positive correlations between SSA (specific surface area) derived from N₂GA experiments and contents of total clay minerals (**A**), chlorite (**B**), illite (**C**), I/S (**D**).

The total SSA can be regarded as the sum of SSAs contributed by various tight rock compositions, and therefore, this work proposes a mathematical model to quantitatively reveal the contributions of various clay minerals to total SSA based on the study of Wang et al. [62]. The compositions of tight rocks are first simplified to four categories: chlorite, illite, I/S, and framework minerals, considering that the SSAs of clay minerals are generally far greater than those of framework minerals. Then, the mathematical model can be written as follows:

$$\left(\sum_{i=1}^{n} \left(SSA_{Ch}W_{(Ch)i} + SSA_{I}W_{(I)i} + SSA_{I/S}W_{(I/S)i} + SSA_{FM}W_{(FM)i} \right) = SSA_{i} \\
W_{(Ch)i} + W_{(I)i} + W_{(I/S)i} + W_{(FM)i} = 1 \\
SSA_{Ch} > 0, SSA_{I} > 0, SSA_{I/S} > 0, SSA_{FM} > 0$$
(8)

where SSA_{Ch} , SSA_I , $SSA_{I/S}$, and SSA_{FM} are the SSAs of chlorite, illite, I/S, and framework minerals per unit weight, respectively; W_{Ch} , W_I , $W_{I/S}$, and W_{FM} are the normalized weights of chlorite, illite, I/S, and framework minerals, respectively; and SSA_i is the total SSA of the *i*th tight rock samples obtained from the N₂GA experiment.

Based on the multiple linear regression method, we can obtain the optimized SSA_{Ch} , SSA_I , $SSA_{I/S}$, and SSA_{BM} of 7.412 m²/g, 6.143 m²/g, 15.520 m²/g, and 0.0061 m²/g, respectively, for the nine studied tight rock samples. The estimated SSAs show fine correlation with measured SSAs, with a R^2 of up to 0.92 (Figure 15), indicating that the proposed mathematical model is feasible and reasonable. Specifically, the contribution of I/S to total SSA is the largest, ranging from 0–83.35% with an average of 60.31% (Table 3), consistent with the good correlation between I/S and SSA in Figure 14D. The next is chlorite and illite, corresponding to a proportion of 7.48%–90.83% and 6.55%–10.74%, averaging 29.92% and 8.68% (Table 3), respectively. Framework minerals make the least contribution to total SSA, which is between 0.15% and 2.63%, with a mean of only 1.09% (Table 3).



Figure 15. Correlation between measured and calculated SSAs for tight rock samples from the Xujiaweizi Rift. The black solid line represents the best match (1:1 line), and the black dashed line is the fitting line of measured and calculated SSAs. SSA = specific surface area.

Total clay minerals, illite, I/S, and chlorite are all positively associated with pore volumes derived from the N₂GA experiments, as evidenced by Figure 16. This is because the N₂GA technique can effectively reveal pore networks below 200 nm in diameter, which are dominantly linked with clay minerals, as identified by SEM images. It is worth noting that the R^2 of chlorite and pore volume is slightly lower than that of illite and of smectite with their respective pore volumes (Figure 16B–D), indicating that illite and I/S may have a more evident effect on the development of intragranular-dominant pore networks with diameter of smaller than 200 nm [23,59].



Figure 16. Positive correlations between pore volume derived from N₂GA experiments and contents of total clay minerals (**A**), chlorite (**B**), illite (**C**), I/S (**D**).

Both the average throat radius (r_a) and maximum connected throat radius (r_d , throat radius corresponding to displacement pressure) derived from the RMIP experiments are also negatively

correlated with three types of clay minerals (Figure 17A–F). Illite usually occurs as pore-bridging in pore-throat space and can effectively segment pores and throats [21]. Pore-lining chlorite wraps the surface of primary intergranular pores resulting in a significant reduction of the pore-throat radius [21]. I/S distributes in pores/throats with discrete particles and can also block the throats to some extent [21]. Hence, all of these three kinds of clay minerals can lower the value of r_d . Evidently, chlorite is the most effective one to reduce r_a and r_d derived from the RMIP experiments. The RMIP experiment is more suitable for revealing pores larger than 240 nm in diameter in this study, and these pores are more closely related to chlorite comprising relatively larger pores.



Figure 17. Negative relationships between average throat radius derived from RMIP experiments and contents of chlorite, illite, I/S (**A**–**C**), and negative associations between maximum connected throat radius derived from RMIP experiments and contents of chlorite, illite, I/S (**D**–**F**).

The integration of N₂GA and RMIP is more advantageous in uncovering the pore volumes of multiple scales, which can give a more reasonable result for this work (Figure 8). With the rising clay mineral contents from #1 to #8, the pore size distribution curves exhibit an increasing trend in the amplitude of a smaller pores section and a declining trend in that of a larger pores section but no evident change in the coverage areas of pore size distribution curves. This again confirms the evolution from intergranular-dominant pore networks to intragranular-dominant pore networks with increasing clay mineral content discussed in the above section. The diminution in the proportion of larger pores and the elevation in that of smaller pores will obviously damage the connectivity of pore networks, resulting in a worse seepage capacity of tight rocks [53]. Compared with clay mineral cements that give rise to the changes of the proportion of different pore networks, mechanical compaction will obviously reduce the absolute size and volume of all pores. For instance, for samples #7, intensely mechanical compaction results in a less proportion of larger pores (>1 µm in diameter), but the proportion of smaller pores (<0.1 µm in diameter) is comparable with that of tight rock samples with similar clay mineral contents (Figure 8), illustrating that the effect of mechanical compaction on smaller pores $(<0.1 \,\mu\text{m}$ in diameter) within clay minerals is not significant, due to the protection of rigid particle support [63].

5.3. Effect of Clay Minerals on Permeability

Neasham [21] has demonstrated that the presence of clay minerals can significantly block pores and throats, which is considered to obviously reduce the permeability of the samples. Total clay minerals, chlorite, illite, and I/S are all negatively related to permeability for studied tight rock samples, as shown in Figure 18, and the effect of chlorite on the decrease of permeability is more evident, compared with illite and I/S. Previous studies have demonstrated that throat size rather than pore size controls the seepage capacity of tight reservoirs, and the permeability is primarily contributed by a small part of relatively larger pore-throat networks [12]. In addition, chlorite generally has a stronger control on the throat radius (Figure 17), and it makes a higher contribution to the intragranular-dominant pore networks of tight gas reservoirs (Figure 12), and thus, its effect on permeability is more obvious.



Figure 18. Relationships between contents of total clay minerals (A), chlorite (B), illite (C), I/S (D), and permeability.

Purcell et al. [64] proposed a method that was used to calculate the contribution of various scales of throats to the permeability based on mercury intrusion data, and this equation can be written as:

$$K_{j} = \frac{\int_{S_{j}}^{S_{j+1}} r_{(S)}^{2} dS}{\int_{0}^{S_{\max}} r_{(S)}^{2} dS}$$
(9)

where K_j is the contribution of throat radius at r_j to permeability; S_j and S_{j+1} are the mercury intrusion saturations at r_j and r_{j+1} , respectively; $r_{(S)}$ is the throat distribution functions; and dS represents the mercury intrusion saturation from r_j to r_{j+1} . S_{max} is the maximum mercury saturation.

The displacement pressure represents the minimum pressure at which the nonwetting phase fluids begin to significantly displace the wetting phase fluids in porous materials. When the mercury intrusion pressure is lower than displacement pressure, mercury will intrude into pores connected to the external surface of rock samples, which cannot form a continuous flow cluster in these isolated and discontinuous pores [65,66]. When the mercury intrusion pressure exceeds displacement pressure, incremental pores will be filled by mercury, generating increasingly continuous flow cluster. Therefore,

the throat radii below the maximum connected throat radius are the primary contributors to the permeability of tight rocks.

The contribution of intergranular-dominant pore networks to the permeability of studied tight rock samples employing Equation (9) is listed in Table 3. For all samples except #9, intergranular-dominant pore networks rather than intragranular-dominant pore networks are the primary contributor to permeability, with a contribution ranging from 62.73% to 93.40%, which agrees with the study of Xi et al. [12]. We also found that with an increasing clay mineral content, the permeability of tight rocks decreases rapidly, while the contribution of intragranular-dominant pore networks to permeability rises speedily. The existence of excess clay minerals will bring about a quick decline of the number of interconnected intergranular-dominant pores, and the fluid has to select the intragranular-dominant pores as their main flow path. This will induce intragranular-dominant pores to play an increasingly significant role in the seepage process, but the absolute permeability value of tight rocks will decrease obviously. For example, the clay mineral content of sample #9 is up to 22 wt.%, with an intergranular-dominant pore proportion of 9.44% (Tables 1 and 3). Although the contribution of intragranular-dominant pore networks to permeability can reach 85.55%, its absolute permeability is only 0.0352 mD (Tables 1 and 3). Thus, compared with intragranular-dominant pore networks, intergranular-dominant pore networks are more crucial in generating a high permeability of tight gas reservoirs.

Based on the above discussion, clay minerals, especially authigenic clay minerals precipitated in intergranular pores and dissolution pores, significantly decreases the permeability of tight gas reservoirs. Nadeau et al. [67] proposed that less than 5% of authigenic I/S can effectively block the pore network and thus obviously reduce the reservoir permeability. Another possible consequence of the precipitation of authigenic clay minerals is that the relatively poor pore networks will result in an increasing risk of formation overpressure, especially for fine-grained sandstone and shale reservoirs. Formation overpressure can help preserve pore space of tight gas reservoirs to some extent, which may contribute to the relatively high porosity of studied tight rock samples with a burial depth of >3500 m (Table 1).

Many permeability prediction equations have been established based on pore structure parameters [68–70], which were obtained from PMIP (pressure-controlled mercury injection porosimetry) and NMR methods, and these prediction equations can be summarized as the following formula:

$$Log(K) = A + BLog(\varphi) + CLog(r_i)$$
(10)

where *K* is permeability; φ is porosity; and r_i is throat radius corresponding to the various total mercury saturation (*i* = 10%–50%). A, B, and C can be determined according to multiple linear regression.

Evidently, there is no significant correlation between total porosity and permeability for the studied tight rocks (Figure 19A). According to the above discussions, permeability of tight rock samples is dominantly contributed by intergranular-dominant pore networks (Table 3), and the positive relationship between intergranular-dominant porosity ($\varphi_{interG.}$), and permeability is closer (Figure 19A). In addition, for tight rocks with various pore structures, the throat dimension corresponding to the same mercury intrusion saturation is significantly different, and it has different control levels on permeability. Thus, r_{ip} (throat radius at inflection point), instead of r_m (maximum connected throat radius), and r_a (average throat radius) were selected to substitute r_i mentioned above to estimate permeability, due to their well positive correlations with permeability (Figure 19B). Based on the multiple linear regression, the permeability estimation results are shown as follows:

$$Log(K) = 0.076 + 0.689 Log(\varphi_{interG.}) + 2.841 Log(r_{ip}) \qquad R^2 = 0.91$$
(11)

$$Log(K) = -0.823 + 0.349Log(\varphi_{interG.}) + 1.293Log(r_m) \qquad R^2 = 0.77$$
(12)

$$Log(K) = -0.96 + 0.991Log(\varphi_{interG.}) + 1.451Log(r_a) \qquad R^2 = 0.81$$
(13)



Figure 19. Correlations between permeability and porosity (**A**) and throat radius (**B**) parameters. InterG.-dominant = intergranular-dominant.

These three permeability estimation equations, Equations (11) to (13), indicate that r_{ip} is more appropriate than r_a and r_m in predicting permeability, as shown in Figure 20. Evidently, r_{ip} is the throat size boundary of intergranular-dominant and intragranular-dominant pore networks, as discussed in Section 5.1, representing the change from conventional pore-throat structures to tree-like pore structures of tight rocks, and the seepage capability of tight sandstones worsens rapidly. r_m and r_a also can reflect throat size distribution characteristic of tight rocks to some extent, and can also be applied to estimated permeability, with a R^2 of 0.77 and 0.81, respectively. However, these two parameters fail to reveal the critical throat size that changes pore structure and the permeability of tight rocks, and thus, their estimation accuracy is worse than that of r_{ip} (Figure 20).



Figure 20. Measured permeability versus estimated permeability using r_{ip} , r_m , and r_a , respectively. The 1:1 line (black dashed line) exhibits the perfect match.

6. Conclusions

(1) Pore networks in tight gas reservoirs can be divided into intergranular-dominant and intragranular-dominant pore networks, based on surface fractal theory and mercury intrusion features. Intergranular-dominant pore networks correspond to the conventional pore-throat structure model that large pores are connected by wide throats, while intragranular-dominant pore networks are characterized by a tree-like pore structure that the narrower throats are connected to the upper-level wider throats like tree branches, and there is no significant difference between pores and throats.

- (2) Clay minerals are the primary contributor to total specific surface area (SSA) of tight gas reservoirs, among which I/S (mixed-layer illite/smectite) contributes to the most, followed by chlorite and illite, and the contribution of framework minerals is the least. Different types of clay minerals exert diverse degrees of influence on pore structures of tight gas reservoirs due to their dispersed model and morphology, and chlorite has the most evident effect on the reduction of the throat radius of tight rocks.
- (3) For tight gas reservoirs, intragranular-dominant pore networks contribute more to the total pore space, while intergranular-dominant pore networks control permeability. Clay minerals, especially authigenic chlorite, can effectively promote the evolution of intergranular-dominant to intragranular-dominant pore networks. Although the above process has little effect on the total pore space, it can significantly decrease the absolute value of permeability.

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References

- Higgs, K.E.; Zwingmann, H.; Reyes, A.G.; Funnell, R.H. Diagenesis, Porosity Evolution, and Petroleum Emplacement in Tight Gas Reservoirs, Taranaki Basin, New Zealand. J. Sediment. Res. 2007, 77, 1003–1025. [CrossRef]
- 2. Dai, J.; Ni, Y.; Wu, X. Tight gas in China and its significance in exploration and exploitation. *Pet. Explor. Dev.* **2012**, *39*, 277–284. [CrossRef]
- 3. Zou, C.; Zhu, R.; Liu, K.; Su, L.; Bai, B.; Zhang, X.; Yuan, X.; Wang, J. Tight gas sandstone reservoirs in China: Characteristics and recognition criteria. *J. Pet. Sci. Eng.* **2012**, *88*, 82–91. [CrossRef]
- 4. Zhang, L.; Xiao, D.; Lu, S.; Jiang, S.; Chen, L.; Guo, T.; Wu, L. Pore development of the Lower Longmaxi shale in the southeastern Sichuan Basin and its adjacent areas: Insights from lithofacies identification and organic matter. *Mar. Pet. Geol.* **2020**, *104662*, 104662. [CrossRef]
- 5. Schmitt, M.; Fernandes, C.; Wolf, F.G.; Neto, J.A.B.D.C.; Rahner, C.P.; Dos Santos, V.S.S.; Rahner, M.S. Characterization of Brazilian tight gas sandstones relating permeability and Angstrom-to micron-scale pore structures. *J. Nat. Gas Sci. Eng.* **2015**, *27*, 785–807. [CrossRef]
- 6. Nelson, P.H. Pore-throat sizes in sandstones, tight sandstones, and shales. *AAPG Bull.* **2009**, *93*, 329–340. [CrossRef]
- 7. Desbois, G.; Urai, J.L.; Kukla, P.A.; Konstanty, J.; Baerle, C. High-resolution 3D fabric and porosity model in a tight gas sandstone reservoir: A new approach to investigate microstructures from mm- to nm-scale combining argon beam cross-sectioning and SEM imaging. *J. Pet. Sci. Eng.* **2011**, *78*, 243–257. [CrossRef]
- 8. Rezaee, M.; Saeedi, A.; Clennell, B. Tight gas sands permeability estimation from mercury injection capillary pressure and nuclear magnetic resonance data. *J. Pet. Sci. Eng.* **2012**, *88*, 92–99. [CrossRef]
- 9. Xiao, D.; Jiang, S.; Thul, D.; Lu, S.; Zhang, L.; Li, B. Impacts of clay on pore structure, storage and percolation of tight sandstones from the Songliao Basin, China: Implications for genetic classification of tight sandstone reservoirs. *Fuel* **2018**, *211*, 390–404. [CrossRef]
- 10. Lai, J.; Wang, G.; Wang, Z.; Chen, J.; Pang, X.; Wang, S.; Zhou, Z.; He, Z.; Qin, Z.; Fan, X. A review on pore structure characterization in tight sandstones. *Earth-Sci. Rev.* **2018**, 177, 436–457. [CrossRef]

- Clarkson, C.; Solano, N.; Bustin, R.; Bustin, A.; Chalmers, G.R.; He, L.; Melnichenko, Y.; Radlinski, A.; Blach, T. Pore structure characterization of North American shale gas reservoirs using USANS/SANS, gas adsorption, and mercury intrusion. *Fuel* 2013, *103*, 606–616. [CrossRef]
- 12. Xi, K.; Cao, Y.; Haile, B.G.; Zhu, R.; Jahren, J.; Bjørlykke, K.; Zhang, X.; Hellevang, H. How does the pore-throat size control the reservoir quality and oiliness of tight sandstones? The case of the Lower Cretaceous Quantou Formation in the southern Songliao Basin, China. *Mar. Pet. Geol.* **2016**, *76*, 1–15. [CrossRef]
- Zhao, H.; Ning, Z.; Wang, Q.; Zhang, R.; Zhao, T.; Niu, T.; Zeng, Y. Petrophysical characterization of tight oil reservoirs using pressure-controlled porosimetry combined with rate-controlled porosimetry. *Fuel* 2015, 154, 233–242. [CrossRef]
- Zhang, L.; Li, B.; Jiang, S.; Xiao, D.; Lu, S.; Zhang, Y.; Gong, C.; Chen, L. Heterogeneity characterization of the lower Silurian Longmaxi marine shale in the Pengshui area, South China. *Int. J. Coal Geol.* 2018, 195, 250–266. [CrossRef]
- Zhang, L.; Lu, S.; Jiang, S.; Xiao, D.; Chen, L.; Liu, Y.; Zhang, Y.; Li, B.; Gong, C. Effect of Shale Lithofacies on Pore Structure of the Wufeng–Longmaxi Shale in Southeast Chongqing, China. *Energy Fuels* 2018, 32, 6603–6618. [CrossRef]
- Chen, L.; Jiang, Z.; Liu, K.; Tan, J.; Gao, F.; Wang, P. Pore structure characterization for organic-rich Lower Silurian shale in the Upper Yangtze Platform, South China: A possible mechanism for pore development. *J. Nat. Gas Sci. Eng.* 2017, 46, 1–15. [CrossRef]
- 17. Chen, S.; Han, Y.; Fu, C.; Zhang, H.; Zhu, Y.; Zuo, Z.; Shangbin, C.; Yufu, H.; Changqin, F.; Han, Z.; et al. Micro and nano-size pores of clay minerals in shale reservoirs: Implication for the accumulation of shale gas. *Sediment. Geol.* **2016**, *342*, 180–190. [CrossRef]
- Ola, P.S.; Aidi, A.K.; Bankole, O.M. Clay mineral diagenesis and source rock assessment in the Bornu Basin, Nigeria: Implications for thermal maturity and source rock potential. *Mar. Pet. Geol.* 2018, *89*, 653–664. [CrossRef]
- 19. Ross, D.J.; Bustin, R.M. The importance of shale composition and pore structure upon gas storage potential of shale gas reservoirs. *Mar. Pet. Geol.* **2009**, *26*, 916–927. [CrossRef]
- 20. Passey, Q.R.; Bohacs, K.; Esch, W.L.; Klimentidis, R.; Sinha, S. From oil-prone source rock to gas-producing shale reservoir-geologic and petrophysical characterization of unconventional shale gas reservoirs. In Proceedings of the International Oil and Gas Conference and Exhibition, Beijing, China, 8–10 June 2010.
- 21. Neasham, J.W. The morphology of dispersed clay in sandstone reservoirs and its effect on sandstone shaliness, pore space and fluid flow properties. In Proceedings of the Annual Fall Technical Conference and Exhibition, Denver, CO, USA, 9–12 October 1977.
- 22. Rahman, M.J.J.; Worden, R.H. Diagenesis and its impact on the reservoir quality of Miocene sandstones (Surma Group) from the Bengal Basin, Bangladesh. *Mar. Pet. Geol.* **2016**, *77*, 898–915. [CrossRef]
- 23. Ji, L.; Zhang, T.; Milliken, K.L.; Qu, J.; Zhang, X. Experimental investigation of main controls to methane adsorption in clay-rich rocks. *Appl. Geochem.* **2012**, *27*, 2533–2545. [CrossRef]
- 24. Cao, Z.; Liu, G.; Zhan, H.; Li, C.; You, Y.; Yang, C.; Jiang, H. Pore structure characterization of Chang-7 tight sandstone using MICP combined with N2GA techniques and its geological control factors. *Sci. Rep.* **2016**, *6*, 36919. [CrossRef] [PubMed]
- 25. Yang, F.; Ning, Z.F.; Zhang, S.D.; Hu, C.P.; Du, L.H.; Liu, H.Q. Characterization of pore structures in shales through nitrogen adsorption experiment. *Nat. Gas Ind.* **2013**, *33*, 135–140.
- Feng, Z.; Yin, C.; Lu, J.; Zhu, Y. Formation and accumulation of tight sandy conglomerate gas: A case from the Lower Cretaceous Yingcheng Formation of Xujiaweizi fault depression, Songliao Basin. *Pet. Explor. Dev.* 2013, 40, 696–703. [CrossRef]
- 27. Zhao, Z.; Xu, S.; Jiang, X.; Lin, C.; Cheng, H.; Cui, J.; Jia, L. Deep strata geologic structure and tight sandy conglomerate gas exploration in Songliao Basin, East China. *Pet. Explor. Dev.* **2016**, *43*, 13–25. [CrossRef]
- 28. Zhang, E.H.; Jiang, C.J.; Zhang, Y.G.; Li, Z.A.; Feng, X.Y.; Wu, J. Study on the formation and evolution of deep structure of Xujiaweizi fault depression. *Acta Petrol. Sin.* **2010**, *26*, 149–157, (In Chinese with English abstract).
- 29. Fu, G.; Wu, W.; Li, N. Controlling effect of three major faults on gas accumulation in the Xujiaweizi faulted depression, Songliao Basin. *Nat. Gas Ind. B* **2014**, *1*, 159–164. [CrossRef]

- Cai, Q.; Hu, M.; Ngia, N.R.; Hu, Z. Sequence stratigraphy, sedimentary systems and implications for hydrocarbon exploration in the northern Xujiaweizi Fault Depression, Songliao Basin, NE China. *J. Pet. Sci. Eng.* 2017, 152, 471–494. [CrossRef]
- Liu, C.; Yin, C.; Lu, J.; Sun, L.; Wang, Y.; Hu, B.; Li, J. Pore structure and physical properties of sandy conglomerate reservoirs in the Xujiaweizi depression, northern Songliao Basin, China. *J. Pet. Sci. Eng.* 2020, 192, 107217. [CrossRef]
- Lu, S.F.; Gu, M.W.; Zhang, F.F.; Zhang, L.C.; Xiao, D.S. Hydrocarbon accumulation stages and type division of Shahezi Fm. tight glutenite gas reservoirs in the Xujiaweizi Fault Depression, Songliao Basin. *Nat. Gas Ind.* 2017, 37, 12–21.
- 33. Li, R.F.; Yang, Y.Q.; Zhang, G.X.; Ruan, X.F. Systematic restoration of eroded thickness by unconformity in Cretaceous of Xujiaweizi in the north of Songliao Basin. *Earth Sci.* **2012**, *37*, 47–54. (In Chinese with English abstract)
- 34. Feng, Z.; Cheng-Zao, J.; Xi-Nong, X.; Shun, Z.; Zi-Hui, F.; Cross, T.A. Tectonostratigraphic units and stratigraphic sequences of the nonmarine Songliao basin, northeast China. *Basin Res.* **2010**, *22*, 79–95. [CrossRef]
- 35. Zhang, P.; Lee, Y.I.; Zhang, J. Diagenesis of tight-gas sandstones in the lower cretaceous denglouku formation, songliao basin, ne china: Implications for reservoir quality. *J. Pet. Geol.* **2014**, *38*, 99–114. [CrossRef]
- 36. Washburn, E.W. The Dynamics of Capillary Flow. Phys. Rev. 1921, 17, 273–283. [CrossRef]
- 37. Yuan, H.H.; Swanson, B.F. Resolving pore-space characteristics by rate-controlled po-rosimetry. *SPE Form. Eval.* **1989**, *4*, 17–24. [CrossRef]
- He, S.L.; Jiao, C.Y.; Wang, J.G.; Luo, F.P.; Zou, L. Discussion on the differences between constant-speed mercury injection and conventional mercury injection techniques. *Fault-Block Oil Gas Field* 2011, *18*, 235–237. (In Chinese with English abstract)
- 39. Gregg, S.J.; Sing, K.S.W.; Salzberg, H.W. *Adsorption, Surface Area, and Porosity*, 2nd ed.; Academic Press: New York, NY, USA, 1982.
- 40. Barrett, E.P.; Joyner, L.G.; Halenda, P.P. The determination of pore volume and area distributions in porous substances. I. Computations from nitrogen isotherms. *J. Am. Chem. Soc.* **1951**, *73*, 373–380. [CrossRef]
- Hoffman, J.; Hower, J.; Scholle, P.A.; Schluger, P.R. Clay mineral assemblages as low grade metamorphic geothermometers: application to the thrust faulted disturbed belt of montana, U.S.A. SEPM Spec. Publ. 1979, 26, 55–79. [CrossRef]
- Pollastro, R.M. Considerations and Applications of the Illite/Smectite Geothermometer in Hydrocarbon-Bearing Rocks of Miocene to Mississippian Age. *Clays Clay Miner.* 1993, 41, 119–133. [CrossRef]
- 43. Bjorkum, N.G.P.A. An Isochemical Model for Formation of Authigenic Kaolinite, K-Feldspar and Illite in Sediments. *J. Sediment. Res.* **1988**, *58*. [CrossRef]
- 44. Ehrenberg, S.N.; Nadeau, P.H. Formation of Diagenetic Illite in Sandstones of the Garn Formation, Haltenbanken Area, Mid-Norwegian Continental Shelf. *Clay Miner*. **1989**, *24*, 233–253. [CrossRef]
- 45. Zhou, Q.; Feng, Z.; Men, G. Present geothermal characteristics and their relationship with natural gas generation in the Xujiaweizi Rift of the northern Songliao Basin. *Sci. China Earth Sci.* **2007**, *37*, 177–188.
- Yuan, G.; Gluyas, J.; Cao, Y.; Oxtoby, N.H.; Jia, Z.; Wang, Y.; Xi, K.; Li, X. Diagenesis and reservoir quality evolution of the Eocene sandstones in the northern Dongying Sag, Bohai Bay Basin, East China. *Mar. Pet. Geol.* 2015, 62, 77–89. [CrossRef]
- 47. Aagaard, P.; Jahren, J.S.; Harstad, A.O.; Nilsen, O.; Ramm, M. Formation of grain-coating chlorite in sandstones. Laboratory synthesized vs. natural occurrences. *Clay Miner.* **2000**, *35*, 261–269. [CrossRef]
- 48. Pang, X.J.; Wang, Q.B.; Feng, C.; Zhao, M.; Liu, Z.B. Differences and Genesis of High-quality Reservoirs in Es1+2 at the Northern Margin of the Huanghekou Sag, Bohai Sea. *Acta Sedimentol. Sin.* **2020**. (In Chinese with English abstract) [CrossRef]
- 49. Brunauer, S.; Deming, L.S.; Deming, W.E.; Teller, E. On a Theory of the van der Waals Adsorption of Gases. *J. Am. Chem. Soc.* **1940**, *62*, 1723–1732. [CrossRef]
- 50. Sing, K.S.; Everett, D.H.; Haul, R.A.W.; Moscou, L.; Pierotti, R.A.; Rouquerol, J.; Siemieniewsha, T. Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity (Recommendations 1984). *Pure Appl. Chem.* **1985**, *57*, 603–619. [CrossRef]

- 51. Yao, Y.; Liu, D.; Tang, D.; Tang, S.; Huang, W.; Liu, Z.; Che, Y. Fractal characterization of seepage-pores of coals from China: An investigation on permeability of coals. *Comput. Geosci.* 2009, 35, 1159–1166. [CrossRef]
- Wang, H.; Liu, Y.; Song, Y.; Zhao, Y.; Zhao, J.; Wang, D. Fractal analysis and its impact factors on pore structure of artificial cores based on the images obtained using magnetic resonance imaging. *J. Appl. Geophys.* 2012, *86*, 70–81. [CrossRef]
- 53. Lai, J.; Wang, G. Fractal analysis of tight gas sandstones using high-pressure mercury intrusion techniques. *J. Nat. Gas Sci. Eng.* **2015**, *24*, 185–196. [CrossRef]
- 54. Pfeifer, P.; Avnir, D. Chemistry in non integer dimensions between 2 and 3, I: Fractal theory of heterogenous surface. *J. Chem. Phys.* **1983**, *79*, 3558–3565. [CrossRef]
- 55. Li, K.; Horne, R.N. Fractal modeling of capillary pressure curves for The Geysers rocks. *Geothermics* **2006**, *35*, 198–207. [CrossRef]
- 56. Sakhaee-Pour, A.; Bryant, S.L. Effect of pore structure on the producibility of tight-gas sandstones. *AAPG Bull.* **2014**, *98*, 663–694. [CrossRef]
- 57. Yuan, G.H.; Cao, Y.C.; Xi, K.L.; Wang, Y.Z.; Li, X.Y.; Yang, T. Feldspar dissolution and its impact on physical properties of Paleogene clastic reservoirs in the northern slope zone of the Dongying Sag. *Acta Pet. Sin.* **2013**, *34*, 853–866, (In Chinese with English abstract).
- 58. Wang, X. Characteristics of clay minerals and their effects on production capacity of the Cretaceous sandstone reservoirs of Songliao Basin, China. *Sci. Géologiques Bull. Mémoires* **1990**, *88*, 105–114.
- 59. Wang, M.Z.; Liu, S.B.; Ren, Y.J.; Tian, H. Pore characteristics and methane adsorption of clay minerals in shale gas reservoir. *Geol. Rev.* 2015, *61*, 207–216, (In Chinese with English abstract).
- 60. Omotoso, O.E.; Mikula, R.J. High surface areas caused by smectitic interstratification of kaolinite and illite in athabasca oil sands. *Appl. Clay Sci.* 2004, 25, 37–47. [CrossRef]
- 61. Boles, S.G.F.J.R. Clay Diagenesis in Wilcox Sandstones of Southwest Texas: Implications of Smectite Diagenesis on Sandstone Cementation. *J. Sediment. Res.* **1979**, *49*. [CrossRef]
- Wang, Y.; Dong, D.; Yang, H.; He, L.; Wang, S.; Huang, J.; Pu, B.; Wang, S. Quantitative characterization of reservoir space in the Lower Silurian Longmaxi Shale, southern Sichuan, China. *Sci. China Earth Sci.* 2013, 57, 313–322. [CrossRef]
- 63. Mbia, E.N.; Fabricius, I.L.; Krogsbøll, A.; Frykman, P.; Dalhoff, F. Permeability, compressibility and porosity of Jurassic shale from the Norwegian–Danish Basin. *Pet. Geosci.* **2014**, *20*, 257–281. [CrossRef]
- 64. Purcell, W. Capillary Pressures—Their Measurement Using Mercury and the Calculation of Permeability Therefrom. *J. Pet. Technol.* **1949**, *1*, 39–48. [CrossRef]
- 65. Katz, A.J.; Thompson, A.H. Quantitative prediction of permeability in porous rock. *Phys. Rev. B* **1986**, *34*, 8179–8181. [CrossRef]
- 66. Daigle, H.; Johnson, A. Combining Mercury Intrusion and Nuclear Magnetic Resonance Measurements Using Percolation Theory. *Transp. Porous Media* **2015**, *111*, 669–679. [CrossRef]
- Nadeau, P.H.; Peacor, D.R.; Yan, J.; Hillier, S. IS precipitation in pore space as the cause of geopressuring in Mesozoic mudstones, Egersund Basin, Norwegian continental shelf. *Am. Miner.* 2002, *87*, 1580–1589. [CrossRef]
- 68. Pittman, E.D. Relationship of Porosity and Permeability to Various Parameters Derived from Mercury Injection-Capillary Pressure Curves for Sandstone (1). *AAPG Bull.* **1992**, *76*, 191–198. [CrossRef]
- 69. Coates, G.R.; Xiao, L.; Prammer, M.G. *NMR Logging Principles and Applications, Halliburton Energy Services Publication H02308*; Halliburton: Houston, TX, USA, 1999.
- 70. Xiao, L.; Mao, Z.-Q.; Wang, Z.-N.; Jin, Y. Application of NMR logs in tight gas reservoirs for formation evaluation: A case study of Sichuan basin in China. *J. Pet. Sci. Eng.* **2012**, *81*, 182–195. [CrossRef]



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