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Matrix Compressibility and Its Controlling Factors of the Marine Shale Gas Reservoir: A Case Study of the Ning228 Well in the Southwest Sichuan Basin, China

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Abstract: Exploring the compressibility of the deeply buried marine shale matrix and its controlling factors can help achieve efficient petroleum production. Taking ten sets of deeply buried marine shale core samples from Ning228 wells in the Yanjin area as an example, the matrix compressibility and pore characteristics of deeply buried marine shale reservoirs were investigated by applying mercury intrusion porosimetry (MIP) and nitrogen adsorption/desorption isotherms at a low temperature of 77 K. Mathematical models (based on MIP and nitrogen adsorption/desorption isotherms) were established to analyze the effects of TOC, mineral components, and pore structure on matrix compressibility. The relationship between the compressibility coefficient and the brittleness index was also established. The results show that the compressibility of the shale matrix is significant when the mercury injection pressure ranges from 8.66 to 37 MPa. For deeply buried marine shale, the matrix compressibility is in the range of 0.23×10^{-4} – 22.03×10^{-4} MPa^{−1}. The influence of TOC and minerals on matrix compressibility is mainly reflected in the control effect of pore structure. High TOC content decreases the overall shale elastic modulus, and high clay mineral content enhances shale stress sensitivity, resulting in a significant matrix compressibility effect. For the effect of pore structure on compressibility, the pore content in shale has a positive effect on matrix compressibility. In addition, the pore-specific surface area is critical to the effective variation of shale matrix compressibility, indicating that the complexity of the shale pore structure is a key factor affecting matrix compressibility.

Keywords: marine shale; matrix compressibility; mercury intrusion porosimetry; low-temperature nitrogen adsorption; brittleness index



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1. Introduction

Shale is a kind of heterogeneous and organic rock composed of matrix and pore fractures [1,2]. Its matrix has a solid particle structure with many micro-pores, and there is a pore fracture system within or between the matrices. The large number of pore spaces serves as the main bearer of shale gas fugacity, which is closely related to shale gas generation and storage capacity. Since shale gas reservoirs are mostly dense porous media with low porosity and ultra-low permeability, conventional natural gas extraction methods cannot achieve commercial exploitation of shale gas. Therefore, hydraulic fracturing technology is often used to artificially fracture shale reservoirs to form more fracture networks in the reservoirs [3,4], thus increasing the transport channels for shale gas seepage. The pore structure and seepage capacity of shale are both highly stress sensitive. As part of the shale gas exploitation process, changes in stress will lead to changes in shale reservoir and matrix volume, which in turn will cause changes in matrix permeability, influencing the

effect of hydraulic fracturing and shale gas production [4–6]. Due to the complexity of shale reservoirs, such changes in volume data are usually not directly available but can be estimated by matrix compressibility.

Two effects can be attributed to the change in volume of the shale reservoir matrix due to stress: the pressure induced effect characterized by matrix compressibility and the desorption effect characterized by shrinkage of the matrix [5,7]. There have been many studies on the effects of matrix shrinkage. However, relatively few studies have been conducted with pressure-induced matrix compressibility in shale reservoirs. Mercury intrusion porosimetry (MIP) is commonly applied to verify pore structure characteristics of shale reservoir, including pore distribution and pore volume [8–10]. In the process of the MIP experiment, the higher mercury injection pressure will cause the destruction of the primary pores of the shale and the compression of the matrix, resulting in a larger amount of incoming mercury than the actual number of pores in the shale, causing a large error [11,12]. Many scholars tend to use the matrix compressibility to calibrate the MIP data [12–14]. Within a certain pressure range, the matrix deformation caused by compression belongs to elastic deformation [10,15], and the deformation caused by compression is linearly correlated with the pressure increment in MIP experiments. Based on this principle, scholars have deduced the calculation formula of the matrix compressibility coefficient for the quantitative study of reservoir matrix compressibility [11,14,16]. Many remarkable and effective results have been achieved in the research process. Previous studies have shown that when the injection pressure of mercury is higher than 10 MPa [14,16,17], the reservoir matrix can be compressed, which also indicates that the data measured by MIP in the high pressure section contain information about the compressibility of rock samples. Li et al. proposed and verified the feasibility of using fractal dimensions to distinguish the matrix compressibility from the pore filling effect in the high-pressure stage of MIP [11]. Guo et al. showed that the effect of different pressure levels on the matrix compressibility is quite small and rather negligible [13]. Han et al. indicated that the matrix compressibility and pore filling effect existed simultaneously at pressures of 10–206 MPa, with the matrix compressibility dominating [10]. Cai et al. determined that the compressibility of the coal matrix varies as the rank of coal changes by applying MIP with the N₂ adsorption isotherm at 77 K [14]. Shale reservoir matrix compression involves lithology, microscopic pore-fracture structure, and fluid characteristics. Previous studies in this area have tended to focus on coal of different ranks and different regions. The quantitative characterization and control factors of the matrix compressibility of marine shale have not been as well covered, and the current status of research in this area is still relatively weak. In particular, deeply buried marine shale has become an important target for shale gas exploration and development in China [18]. Therefore, based on the experience and results of previous studies on the compressibility of the coal matrix, we apply the kerogen vitrinite reflectance test, the total organic carbon (TOC) test, X-ray diffraction whole-rock quantitative analysis, mercury intrusion porosimetry (MIP), and low-temperature liquid nitrogen adsorption experiments to achieve quantitative characterization and qualitative analysis of the matrix compressibility of deeply buried marine shale and its influencing factors by using marine shale core samples from the Ning228 well in the southwestern Sichuan basin, China.

This paper proposes a theoretical method for assessing the matrix compressibility of shale reservoirs and establishes the interrelationship between organic matter, mineral fraction, pore structure, and shale matrix compressibility, with the goal of providing some theoretical basis for efficient shale gas production. Distinguishing features of this work include the following: (1) the evaluation of matrix compressibility of deep marine shale; (2) the microscopic pore structure assessment of shale using MIP combined with the N₂ adsorption isotherm at 77 K; (3) factors that influence the compressibility of the deep marine shale matrix.

2. Samples and Methodology

2.1. Regional Overview and Sample Analysis

Yanjin is a key area for the exploration and exploitation of shale gas in Yunnan Province. It lies on the southwestern edge of the Sichuan Basin, in a restricted–semi-confined paleogeographic pattern formed by the combination of the Chuanzhong Uplift, the Qianzhong Uplift, and the Kangdian Archicontinent (Figure 1a). Under this pattern, transgression and regression events have occurred successively; then, the black shale of the Lower Silurian Longmaxi Formation, which has a broad distribution, and is thick and rich in organic matter, has been studied [19,20]. The Longmaxi Formation is distributed in the area north of Zhenxiong and Yiliang counties, and its stratigraphy has been subjected to different degrees of uplift and denudation due to late tectonic movements. In general, the Longmaxi Formation in the Daguan–Yanjin–Suijiang region has a relatively small denudation area, more outcrop distribution, and less and sparse distribution of faults and folds; it is an essential area for research and development of shale gas reservoirs [20–22] (Figure 1b). The Yanjin area focuses on the development of two series of marine shale from the Lower Paleozoic, the Lower Cambrian Qiongzhusi Formation, and the Upper Ordovician Wufeng Formation–Lower Silurian Longmaxi Formation. The main formation discussed in this paper is the Longmaxi Formation of Lower Silurian in the Yanjin Ning228 well.

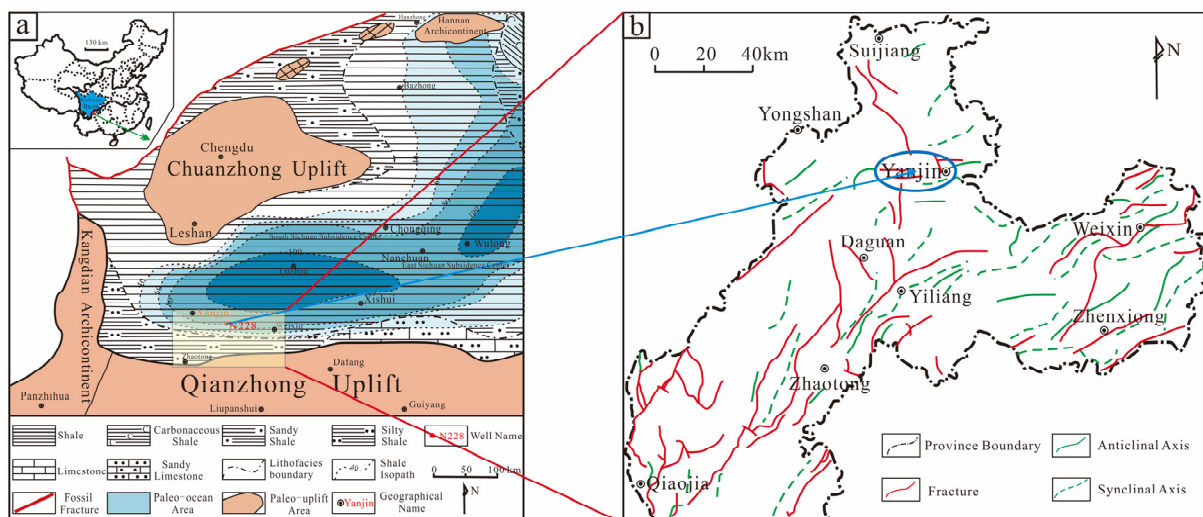


Figure 1. Palaeogeography map [19] (reproduced with permission from author, Journal of Palaeogeography, 2021) (a) of the Late Ordovician–Early Silurian in southwestern Sichuan Basin and the structure distribution map [22] (reproduced with permission from author, Natural Gas Geoscience, 2015) (b) of the Yanjin block.

The samples were collected from the Ning228 well in the Yanjin block, and ten sets of shale core samples were selected from the Longmaxi Formation in the depth range of 3365 m to 3465 m. According to the SY/T 5124-2012 standard procedure [23], the GB/T 19145-2022 standard procedure [24], and the SY/T 5163-2010 standard procedure [25], the basic experimental tests, including the kerogen vitrinite reflectance ($R_{o,m}$) test, the total organic carbon (TOC) test, and X-ray diffraction (XRD) whole-rock quantitative analysis were conducted, respectively. The $R_{o,m}$ test was conducted by using the vitrinite reflectance tester model QDI302 produced by Craic. The kerogen was first prepared from the original shale core; then, the vitrinite reflectance analysis was conducted with the measurement point of asphalt. The TOC test is based on the principle of the combustion method using C-744 carbon and sulfur analyzers. Before starting, the shale sample was crushed to a particle size of less than 0.2 mm, and after removing the inorganic carbon from the sample with dilute hydrochloric acid, the sample was burned and oxidized at high temperature

to convert the organic carbon into CO₂. Then, the CO₂ volume was detected with a thermal conductivity detector, and the TOC value of shale samples can be converted. The X-ray diffraction whole-rock quantitative analysis was performed with a Rigaku Ultima IV X-ray diffractometer with an operating voltage of 20 kV–40 kV and a scanning current of 10 mA–40 mA, which were mainly used to determine the mineral species based on the crystal structure of the scanned samples and to determine the level of phase content based on the strength of the diffraction peaks. Here, the basic information of the samples was obtained, as shown in Table 1.

Table 1. Sample information and basic parameters of the selected Longmaxi shale.

Sample No.	Depth (m)	R _{o,m} (%)	TOC (%)	Mineral Content (%)					
				Quartz	Feldspar	Calcite	Dolomite	Pyrite	Clay Minerals
N228-1	3365.10	4.45	1.456	27.10	9.00	20.00	3.90	0.60	39.40
N228-13	3376.81	4.10	1.46	25.00	6.30	28.00	3.50	0.90	36.30
N228-24	3387.99	4.18	2.055	28.30	4.30	3.60	0.00	1.00	62.70
N228-35	3398.71	4.40	1.729	30.10	6.90	18.10	4.20	0.80	39.90
N228-46	3409.93	4.20	1.973	35.60	5.40	8.90	0.00	1.70	48.40
N228-57	3420.96	4.38	1.531	36.20	5.80	6.10	0.00	0.60	51.50
N228-67	3431.09	4.18	1.783	35.60	10.90	10.90	0.00	0.80	41.70
N228-78	3442.25	4.60	1.642	42.40	11.40	10.30	1.60	0.80	33.30
N228-88	3452.79	4.32	4.248	34.00	4.40	9.00	0.00	1.40	51.10
N228-100	3465.08	4.60	4.233	63.30	3.90	11.40	2.40	1.40	17.60

2.2. Mercury Intrusion Porosimetry and Nitrogen Adsorption/Desorption

Mercury intrusion porosimetry (MIP) is a conventional pore characterization technique that is widely used to determine the size distribution of pores in porous materials. It is suitable for conventional and unconventional reservoirs, which can obtain pore data such as pore volume, pore size distribution, and pore throat connectivity of samples [10,14,26]. The MIP analysis was conducted using an American Autopore 9500 Instrument (Micromeritics, US) in accordance with the standard procedure of GB/T 29171-2012 [27] at Sichuan Koyuan Engineering and Technology Testing Center. The experimental pressure can reach up to 228 MPa, and the measurable pore size range is 5 nm to 1000 µm. At each pressure point, when the capillary pressure equilibrium is reached in the rock samples, the injected pressure and the inlet mercury data are recorded at the same time; then, the sample pressure–mercury curves can be plotted [28]. The MIP curves of ten groups of shale samples were obtained, as shown in Figure 2. Based on the Washburn equation [29], it is possible to calculate the pore size of shale samples by combining mercury injection parameters. Here, we take the contact angle between the sample surface and the mercury vapor to be 140 °C, and the surface tension of mercury is fixed at 0.48 N/m in the experiment. In addition, the low-temperature N₂ adsorption/desorption experiment is a more common technique for testing pore structure both domestically and internationally. Different from the mercury pressure experiment, the former tests a broad range of pore sizes, which is suitable for reflecting the distribution of medium and large pores, while the low-temperature N₂ adsorption/desorption experiment can measure pores with a smaller pore size range and is suitable for characterizing the structural parameters of micropores. The low-temperature (77 K) N₂ adsorption/desorption experiment was performed using the Micromeritics ASPA 2460 system at Sichuan Keyuan Engineering Technology Testing Center, following the standard GB/T 19587-2017 procedure [30]. The range of pore sizes tested is 1.7 to 300 nm. Its basic principle is that under the condition of constant temperature, the adsorption capacity V is a function of nitrogen relative pressure (equilibrium pressure P /saturation vapor pressure P_0) when nitrogen reaches adsorption equilibrium on the shale surface. Therefore, the amount of nitrogen adsorption can be determined by the magnitude of the relative pressure, so the pore structure parameters such as pore volume and pore specific surface area of all samples are known. The N₂ adsorption/desorption curves of all samples

at 77 K were acquired as shown in Figure 3. Compared with conventional reservoirs, the pore size of the shale reservoir is extremely small, with more complex pore size distribution and pore genesis. Its pore structure also has strong non-homogeneous characteristics, so there is still no unified standard terminology system for the classification of shale gas micro-reservoir space. In this paper, the shale reservoir space is divided into micropores (<2 nm), mesopores (2–50 nm), and macropores (>50 nm) by IUPAC (1982) [31].

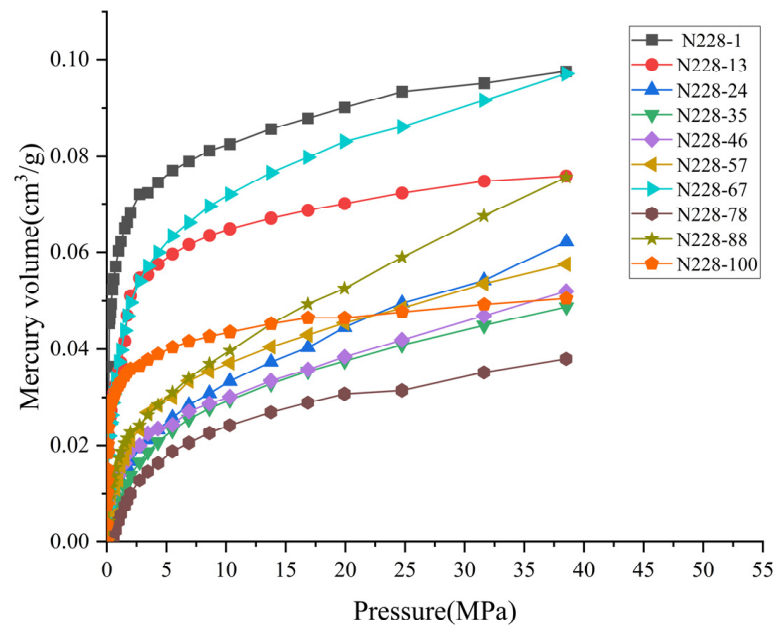


Figure 2. MIP curves of different buried depths.

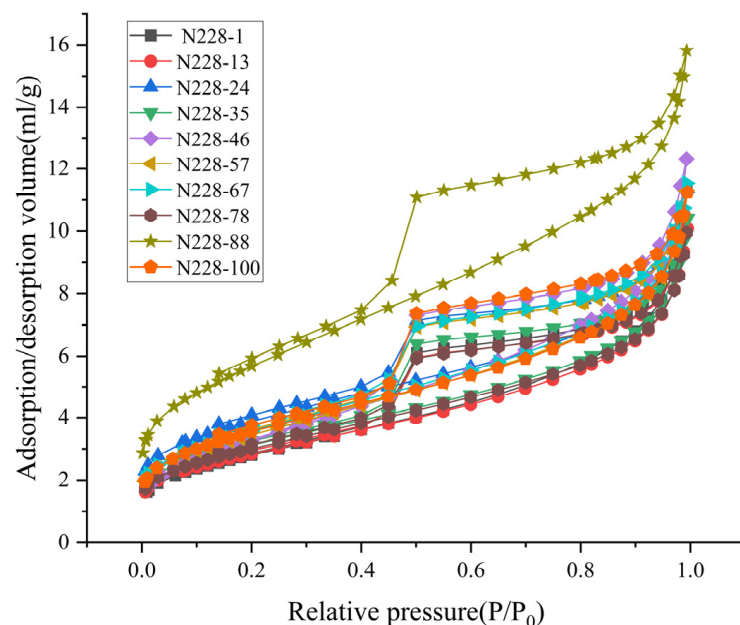


Figure 3. N₂ adsorption/desorption at low temperature (77 K) of different buried depths.

2.3. Shale Matrix Compressibility

For rocks, mercury is a fluid that is non-wetting phase. It is only when the pressure applied to mercury is greater than or equal to the capillary pressure of the pore throat that mercury is able to overcome the capillary resistance to penetrate the pore [28]. When

applying the Washburn equation [29] to obtain the pore radius, it is generally assumed that the pore shape of the sample is cylindrical. The calculation is shown in Equation (1):

$$P_c = -\frac{2\sigma \cos \theta}{r_c} \quad (1)$$

where σ represents the surface tension of mercury (N/m); θ is the wetting contact angle from the sample to mercury ($^\circ$); P_c is the inlet pressure of mercury (MPa); and r_c represents the radius of the capillary (μm) at the respective pressure. Here, we set σ to 0.48 N/m and θ to 140° . The equation can be simplified as

$$P_c = \frac{0.735}{r_c} \quad (2)$$

Based on Equation (2), the corresponding pore radius can be obtained from the mercury injection pressure. Then, the pore volume of the corresponding pore diameter can be analyzed according to the amount of mercury injection.

If mercury compressibility is neglected, the shale matrix compressibility can be defined as [10,11]

$$C_m = \frac{dV_m}{V_m dP} \quad (3)$$

where dV_m/dP is the volume change of the shale matrix as a function of pressure, V_m is the shale matrix volume, and P is the fluid pressure.

The shale matrix volume V_m can be defined as

$$V_m = \frac{1}{\rho} - V_T \quad (4)$$

where ρ is the density of shale samples (g/cm^3), which represents the reciprocal of the total volume of the shale sample; and V_T (cm^3/g) is the BJH pore volume [32], which represents the total pore volume of shale samples and can be calculated from low-temperature nitrogen adsorption experimental data. The BJH theory is based on the theory of multilayer adsorption by BET and the phenomenon of gas-phase capillary coalescence in porous materials [32]. In order to obtain the BET pore area, BJH pore volumes, and pore size distributions of the shale samples, nitrogen adsorption and desorption isotherms were measured over the relative pressure range of 0.01–0.99 MPa.

In MIP, with increasing mercury intrusion, significant compression can be detected in shale. In the case of compressible porous solids, a relation like Equation (5) exists:

$$\Delta V_{\text{mercury}} = \Delta V_{\text{pore}} + \Delta V_{\text{compaction}} \quad (5)$$

where $\Delta V_{\text{mercury}}$ is the mercury injection volume, ΔV_{pore} is the pore volume, and $\Delta V_{\text{compaction}}$ is the matrix compression volume. This formula indicates that the observed mercury volume increment comes from pore filling ΔV_{pore} and solid compression $\Delta V_{\text{compaction}}$, respectively.

Drawing on the experience and achievements of previous studies on the compressibility characteristics of the coal matrix [11,14,16], the pressure is set in the range of 8.66 MPa to 37 MPa, corresponding to the interstitial interval of 170 nm to 40 nm (Equation (2)). It can be found that when the experimental pressure is 8.66–37 MPa, the mercury injection volume and pressure show a better linear relationship that is approximately linear by observing the curve of cumulative mercury volume at different pressures (Figure 2). The shale pore fracture space is filled with incompressible mercury. Prior studies have demonstrated that for shale samples with a pore size of diameters < 200 nm, neither sample size nor particle size has a significant effect on the evaluation of pore structure. Therefore, we can assume that the ratio of mercury injection volume to pressure is constant N in this pressure section, while the volume change of pore-filled mercury at this stage can be approximated by the pore volume with the pore diameter ranging from 40 to 170 nm. Therefore, the change

in mercury injection volume observed at this stage is equal to the sum of the compressed volume of the shale matrix and the pore-filled volume with a pore diameter of 40–170 nm. Thus, we can approximate Equation (6):

$$\frac{\Delta V_{\text{compaction}}}{\Delta P} = N - \frac{\sum_{40\text{nm}}^{170\text{nm}} \Delta V_{\text{pore}}}{\Delta P} \quad (6)$$

When the pores of the sample remain constant during the compression process, $\Delta V_{\text{mercury}}/\Delta P$ or $\Delta V_{\text{compaction}}/\Delta P$ is valid. Assuming that $\Delta V_{\text{mercury}}/\Delta P$ or $\Delta V_{\text{compaction}}/\Delta P$ is independent of pressure, we can replace dV_m/dP with $\Delta V_{\text{compaction}}/\Delta P$ and combine Equations (3) and (6). The equation for the shale matrix compression coefficient can be obtained as

$$C_m = \frac{1}{V_m} \left(N - \frac{\sum_{40\text{nm}}^{170\text{nm}} \Delta V_{\text{pore}}}{\Delta P} \right) \quad (7)$$

2.4. Brittleness Index Calculation and Lithofacies Classification

2.4.1. Shale Brittleness Index

The brittleness characteristics of the shale reservoirs have significant implications for shale gas development. Typically, the brittleness index is used to quantitatively calculate and describe the brittleness characteristics of shale. There are numerous methods for calculating the brittleness index, while mineral components are often used to evaluate rock brittleness in China [33–35]. Not only do the type and content of brittle minerals such as quartz, feldspar, and dolomite affect the brittleness of the shale, but they are also related to the ease of fracturing at the final extraction step [36,37]. The better the brittleness of the shale reservoir, the easier a fracture network can be formed during fracturing and the higher the shale gas productivity. On the contrary, the worse the brittleness is, the more obvious the plasticity of the shale will be, which will lead to poor fracturing effects. The evaluation of brittleness using rock mineral fraction characteristics is a method proposed and developed by the Weatherford Company [38], which mainly determines the sample mineral fraction using the whole-rock XRD experiment. Taking quartz as the main brittle mineral, the rock brittleness index can be calculated using XRD data. The calculation formula is shown in Equation (8). This practical method is relatively narrow, and it was later promoted and extended by scholars using the ratio of quartz, feldspar, and brittle carbonate minerals to the total amount of minerals as the brittleness index. Its calculation is shown in Equation (9). This type of method is more comprehensive in characterizing the brittleness characteristics in shale with more complex mineral composition. Therefore, Equation (9) is used to calculate the brittleness index of shale samples in this study.

$$BRIT = \frac{V_{\text{quartz}}}{V_{\text{quartz}} + V_{\text{calcite}} + V_{\text{clay minerals}}} \quad (8)$$

where *BRIT* is the brittleness index (%) and *V* is the mineral content (%).

$$BRIT = \frac{V_{\text{quartz}} + V_{\text{feldspar}} + V_{\text{carbonate minerals}}}{V_{\text{total minerals}}} \quad (9)$$

where V_{feldspar} is the sum of potassium feldspar and plagioclase mineral content (%) and $V_{\text{carbonate minerals}}$ is the sum of calcite and dolomite mineral content (%).

2.4.2. Shale Lithofacies Classification

Shale lithofacies are important for studying shale reservoirs. Scholars often analyze the depositional environment and depositional processes of sedimentary rocks by lithofacies classification. This paper mainly uses lithofacies classification to characterize lithological characteristics of shale. There is still no unified standard for shale lithofacies classification. This work mainly draws on the three-terminal element method of shale formation

lithofacies classification proposed by Wang et al. to petrographically delineate the shale samples of the Longmaxi Formation in the Ning228 well [39]. This method mainly uses data from the whole-rock XRD experiment to establish a triangular plate composed of quartz + feldspar, carbonate (e.g., calcite + dolomite), and clay. Then, based on sedimentary petrological classification criteria, the shale lithofacies are divided into six petrographic zones according to the principle of equal probability of the same pattern, e.g., siliceous shale, clay shale, calcareous shale, clay siliceous mixed shale, clay calcareous mixed shale, and calcareous siliceous mixed shale. The latter three are all mixed shale facies. The specific criteria for the division are shown in Table 2.

Table 2. Classification scheme of lithofacies types of marine shale.

Lithofacies Types		Percentage of Shale Mineral Components (%)		
		Quartz + Feldspar	Carbonate	Clay
	Siliceous shale	50~75	<30	10~50
	Clay shale	25~50	<30	50~75
	Calcareous shale	<30	50~75	25~50
Mixed shale facies	Clay siliceous mixed shale	30~50	<33	30~50
	Clay calcareous mixed shale	<33	30~50	30~50
	Calcareous siliceous mixed shale	30~50	30~50	<33

3. Results

3.1. Shale Characteristics

The ten sets of shale core samples from the Ning228 well in the Yanjin area are all marine over-mature hydrocarbon source rocks, and their maximum vitrinite reflectance is greater than 4%. Previous studies have shown that the maturity of shale in the Lower Paleozoic in southern China is generally high, with $R_{o,m}$ varying from 2% to 5%. Even though their thermal evolution is high, they still maintain a certain degree of porosity [40]. Samples with high maturity can still be used for matrix compressibility studies. The organic matter abundance of all samples is large, with a TOC content between 1.456% and 4.248%, in a mean of 2.211%. With the increase of burial depth, it shows that the typical characteristics in the lower section are high, and in the upper section, they are low, which is mainly related to the sedimentary background of the Longmaxi Formation in the Yanjin area [20,41,42]. The mineral fraction varies widely, with the highest content of clay minerals ranging from 17.6% to 62.7% with a mean of 42.19%; the quartz content is the second highest, ranging from 25% to 63.3%, with an average of 35.76%; calcite and feldspar (potassium feldspar and plagioclase) are less abundant, ranging from 3.6% to 28% and 3.9% to 11.4%, respectively, accounting for 12.63% and 6.63% of the total proportion. In addition, there is some dolomite and pyrite.

Both quartz and pyrite show a good dependence on TOC from the vertical upward. Figure 4 shows that the TOC content increases significantly with the increase of quartz and pyrite content. Meanwhile, the quartz and pyrite contents show an overall increasing trend with increasing burial depth. Closer to the bottom of the Longmaxi Formation, the quartz and pyrite contents increase steeply with larger TOC values to reach the peak. Previous studies have shown that both silica-rich and pyrite-rich mineralogical characteristics indicate a reductive deep-water depositional environment favorable for organic matter enrichment [43], suggesting that a set of high-quality silica-rich hydrocarbon source rocks were deposited in the lower part of the Longmaxi Formation in the Ning228 well.

3.2. Pore Structure Characteristics from Mercury Intrusion Porosimetry

The experimental analysis shows that mesopores are the main component of the pores in the Longmaxi Formation shale of the Ning228 well (Figure 5). The volume fraction of

mesopores ranges from 29.64% to 73.75%, with a mean of 55.33%. The average pore volume fraction of macropores is 44.67%. The size of shale pores tends to decrease with increasing burial depth, with the number of mesopores gradually increasing and the number of macropores gradually decreasing. This is mainly related to the special ‘three high’ formation environment of deep reservoirs, namely, high ground stress, high formation temperature, and high reservoir pressure [44]. This special geological environment has a great influence on the pore-fracture structure of shale. The results of mercury injection pore structure analysis of all shale samples at different burial depths are shown in Table 3. The porosity of the shale samples at different burial depths is found to be highly variable, between 1.04% and 7.01%. The maximum mercury saturation and mercury withdrawal efficiency also vary widely, ranging from 7.63% to 31.58% and 25.64% to 77.65%, respectively. This is obviously related to the development of macropores and microfractures in shale. Previous research has revealed that the mercury withdrawal efficiency can effectively reflect the connectivity of pores and fractures, thus affecting the permeability of the shale reservoir. In general, the higher the mercury withdrawal efficiency, the more uniform the pore structure and the better the connectivity, which is conducive to the diffusion and infiltration of the shale gas.

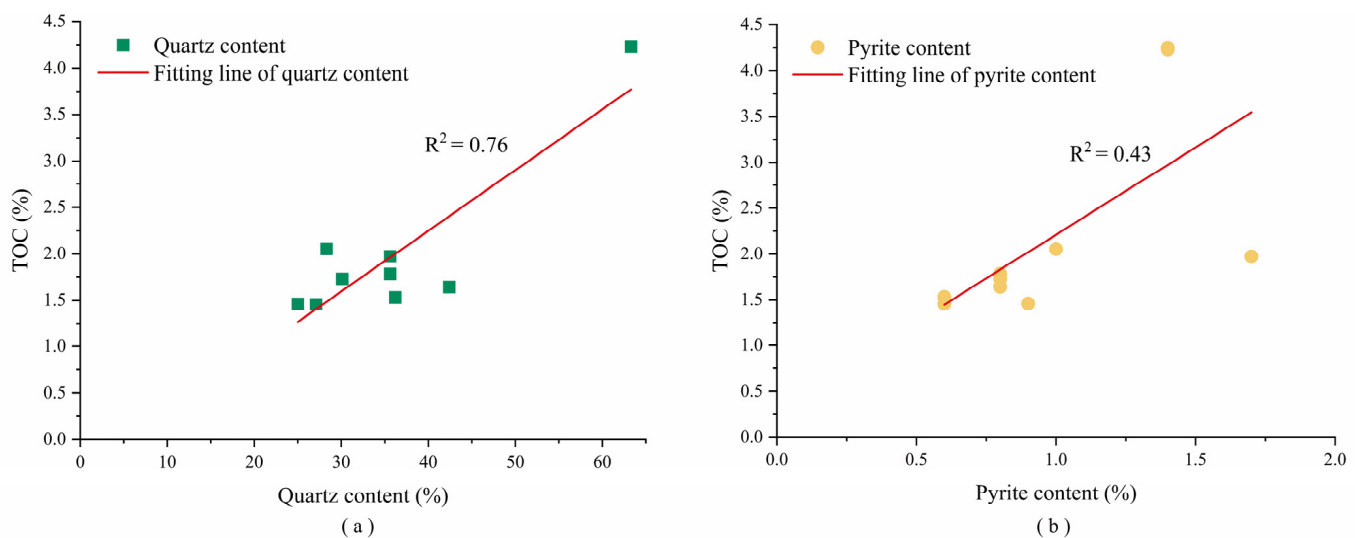


Figure 4. Variation of TOC with quartz and pyrite content. (a) Significant positive linear correlation between TOC and quartz content. (b) Positive linear correlation between TOC and pyrite content.

Table 3. Pore structure characteristics of shale with different buried depths by MIP.

Sample No.	Porosity (%)	Maximum Mercury Saturation (%)	Mercury Withdrawal Efficiency (%)	Total Pore Volume ($\times 10^{-3} \text{ cm}^3/\text{g}$)	Percentage Content of Pores in Different Pore Sizes (%)			Mercury Injection Curve Type
					<2 nm	2–50 nm	>50 nm	
N228-1	2.01	19.39	37.52	7.74	0.00	37.72	62.28	I
N228-13	1.04	26.00	25.64	3.95	0.00	29.64	70.36	I
N228-24	2.00	21.85	72.82	7.66	0.00	70.44	29.56	II
N228-35	2.64	10.56	64.86	10.25	0.00	62.22	37.78	III
N228-46	1.81	20.53	71.67	6.98	0.00	70.76	29.24	II
N228-57	1.86	18.28	67.56	7.13	0.00	62.84	37.16	II
N228-67	1.36	31.58	51.54	5.20	0.00	47.62	52.38	II
N228-78	1.17	18.87	57.57	4.49	0.00	62.91	37.09	II
N228-88	7.01	7.63	77.65	29.68	0.00	73.75	26.25	III
N228-100	1.22	15.28	31.62	4.83	0.00	35.40	64.60	I

In addition, the mercury intrusion curves for all samples are highly variable (Figure 6). Previous studies have shown that the different mercury intrusion curve patterns reflect the variability of pore connectivity and pore size distribution in the shale reservoir. The mercury intrusion curves for all shale samples presented in this paper are further subdivided into three typical types based on the shape of the mercury injection curve.

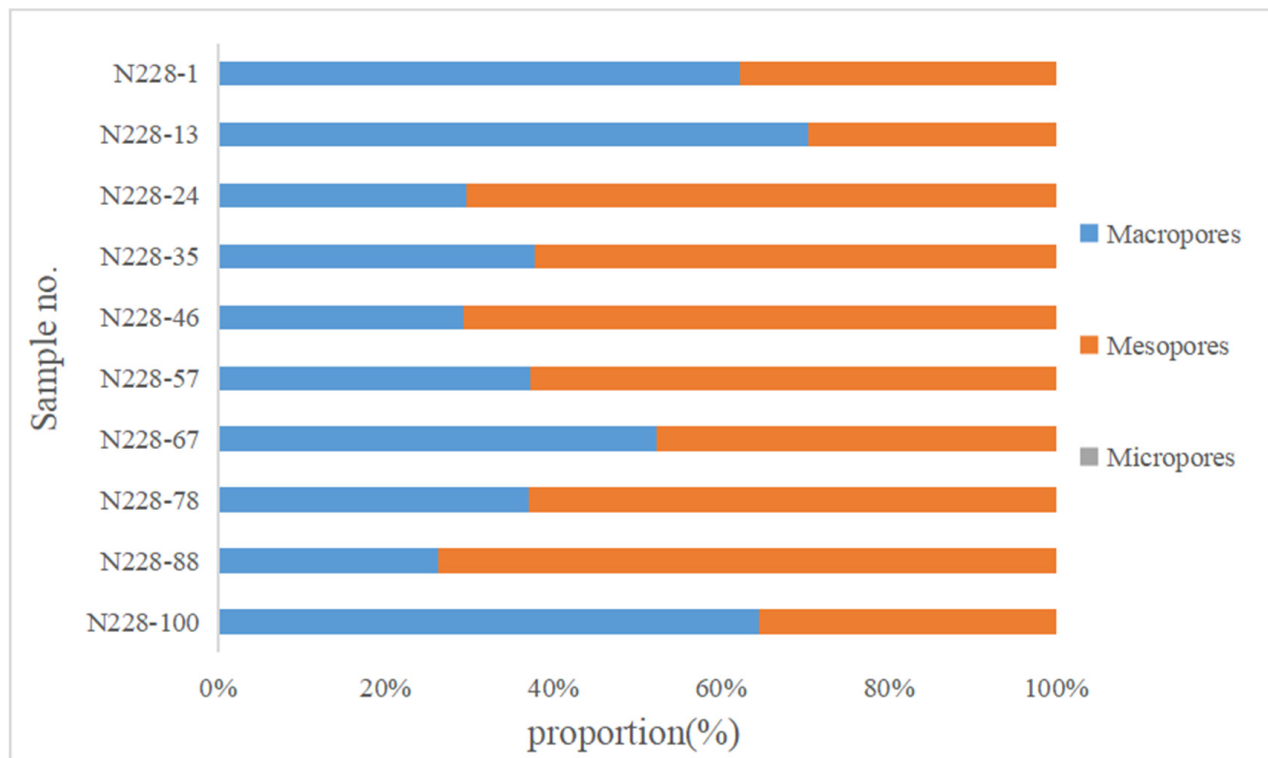
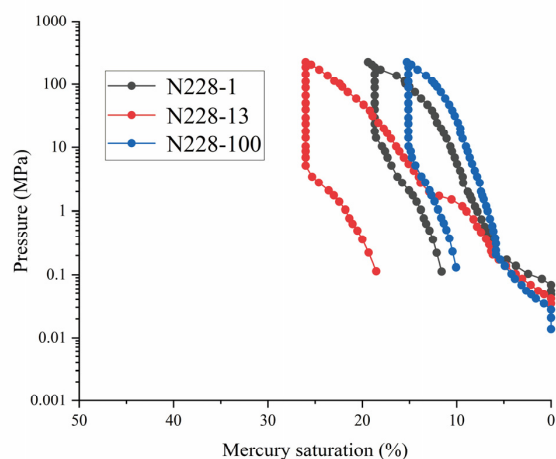


Figure 5. Pore volume distribution of selected shale samples at different sizes from MIP data.

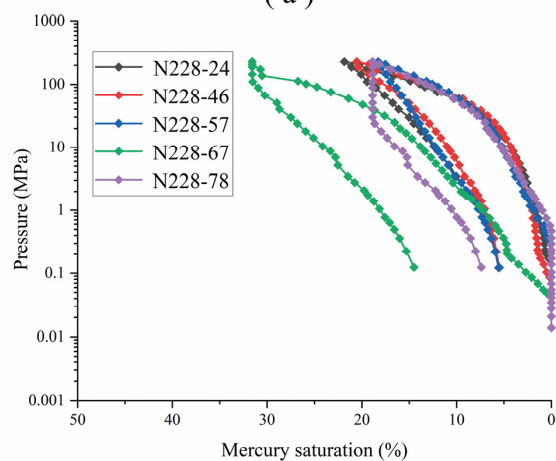
There are three samples of the type (I) curve, accounting for 30% of the total number of samples. The mercury injection curve is a three-stage distribution of “front steep–middle slow–back steep”. When the pressure is less than 1 MPa, there is a steeper oblique section; when the pressure is between 1 and 2 MPa, it is a slower oblique section; when the pressure is greater than 2 MPa, there is a steeper oblique segment. Its maximum mercury saturation is between 15.28% and 26.00%, and the mercury withdrawal efficiency is generally about 31.58%. In addition, when the pressure is less than 0.05 MPa, the curve is approximately a straight line, indicating that mercury is almost not introduced at this stage. The pore structure of the shale reservoir represented by the type (I) curve is extremely unevenly developed, and the connectivity between pores is common.

There are five samples of the type (II) curve, accounting for 50% of the overall number of samples. The mercury injection curve is a two-segment type of “steep at the front and slow at the back”. This means that when the pressure is below 30 MPa, there is a steeper obliquity segment, and when the pressure is greater than 30 MPa, it shows a gentle slash segment. The maximum mercury saturation is 18.28–31.58%, and the mercury withdrawal efficiency is generally about 64.23%. When the pressure is less than 1 MPa, the curve is approximately linear, indicating almost no mercury is introduced at this stage. The pore structure of the shale reservoir represented by the type (II) curve is better developed, with better connectivity. Its micropore content is significantly higher compared with the previous type of mercury intrusion curve.

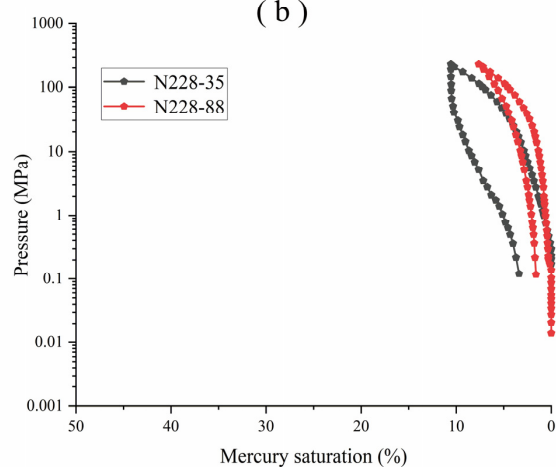
There are only two samples of the type (III) curve, accounting for 20% of the overall number of samples. The overall mercury injection curve is a nearly smooth curve, indicating that the mercury injection is slow and stable. Its maximum mercury saturation is 7.63%–10.56%, in general, and the mercury withdrawal efficiency is about 71.26%. The pore development of shale samples with such curves is uneven, and their micropores are more developed with good pore connectivity.



(a)



(b)



(c)

Figure 6. Three different types of mercury intrusion curves of selected shale samples. (a) The type (I) curve is a three-stage distribution of “front steep–middle slow–back steep”, accounting for 30% of the total number of samples. (b) The type (II) curve is a two-segment type of “steep at the front and slow at the back”, accounting for 50% of the overall number of samples. (c) The type (III) curve is a nearly smooth curve, accounting for 20% of the overall number of samples.

3.3. Pore Structure Characteristics from N_2 Adsorption/Desorption at 77 K

Figure 3 shows that the selected shale samples in this experiment all form hysteresis loops. There is no overlap between the adsorption and desorption curves of the samples in the $P/P_0 > 0.5$ relative pressure part. The formation of hysteresis loops denotes that the pores in the Longmaxi Formation shale reservoir within the study area are mostly open pores, which are mainly cylindrical pores, conical pores, and parallel plate-like pores with both ends open [45–47]. The adsorption curves have the characteristics of both the type H3 loop and the type H4 loop recommended by IUPAC, which show that the adsorption curves are steep near the saturation vapor pressure and the desorption curves are steep at medium pressure. The rising rate of the adsorption curves is closely related to the openness of the open pores, and the steeper adsorption curve indicates a greater degree of pore opening. None of the samples reaches saturation adsorption at relative pressures close to 1, indicating that capillary condensation occurs [48]. At a relative pressure of 0.5, there is a clear inflection point on the adsorption curve, indicating the presence of a certain amount of fine-necked vial pores in the sample.

The results from the low-temperature N_2 adsorption experiment show that the pore-specific surface area of the selected samples ranges from 10.0153 to 20.5537 m^2/g , with an average specific surface area of 12.4607 m^2/g . With the increase of buried depth, there is a tendency for the specific surface area of the shale samples to increase and then decrease. Shale samples vary in pore volume from 0.0163 to 0.0263 cm^3/g , with a large variation in pore volume among different samples. Figure 7 shows that the specific surface areas of mesopores and micropores account for 81.99% and 17.23% of the total specific surface area, respectively. As shown in Figure 8, the pore volumes of mesopores and macropores account for 79.28% and 14.54% of the total pore volume, respectively. Mesopores provide the majority of the shale gas storage space, which means that mesopores are the main component of the pores in the Longmaxi Formation shale of the Ning228 well. However, the average pore volume of mesopores measured by MIP is 55.33%, which is 23.95% different from the measured value of the low-temperature N_2 adsorption experiment. This is a big difference. The main reason is that the matrix pores of shale reservoirs are easily damaged under high pressure due to the matrix compressibility, resulting in lower accuracy of pore characterization below 50 nm in mercury intrusion porosimetry [49]. The low-temperature nitrogen adsorption has no destructive effect on pores, and it has an excellent characterization effect on nano-scale pores. This shows that the MIP and low-temperature N_2 adsorption have their own advantages and complementarity in shale pore structure characterization.

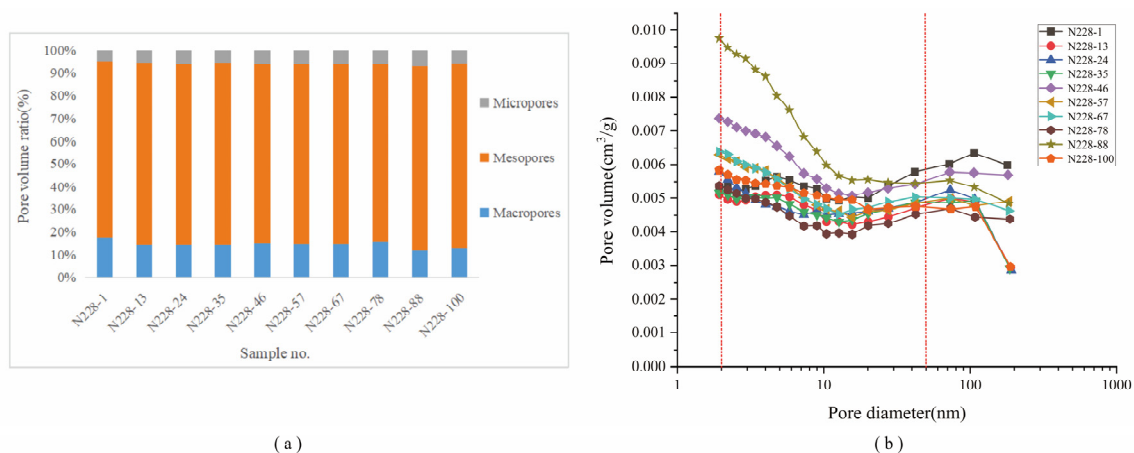


Figure 7. Specific surface area distribution of selected shale samples with different buried depths. (a) Histogram of pore volume distribution of shale samples with different pore types. (b) Pore volume distribution of shale samples with different pore size ranges.

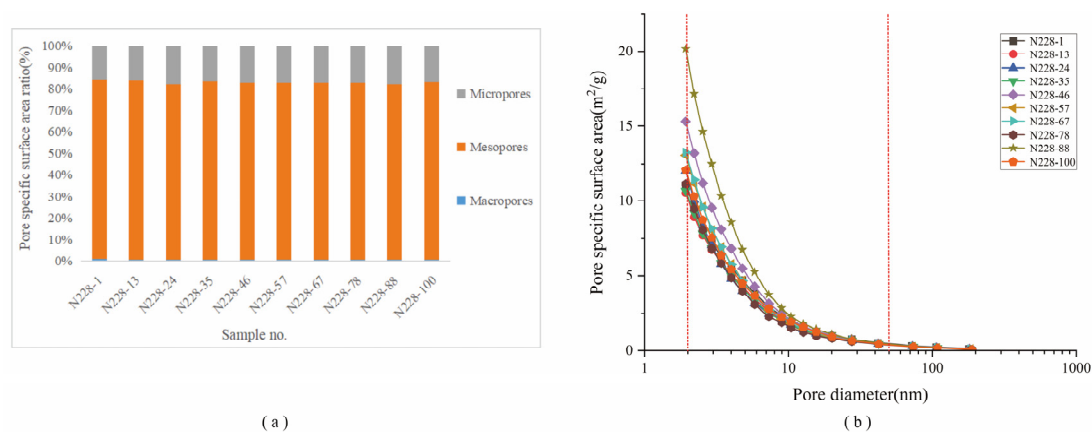


Figure 8. Pore volume distribution of selected shale samples with different buried depths. (a) Histogram of pore specific surface area distribution of shale samples with different pore types. (b) Distribution of pore specific surface area of shale samples with different pore size ranges.

3.4. Calculated Shale Matrix Compressibility

Consistent with the MIP and low-temperature N_2 adsorption/desorption data, the matrix compression coefficients of the ten shale samples with pore sizes of approximately 40 to 170 nm were calculated, as shown in Table 4. In the pressure interval of 8.66–37 MPa, the mercury injection volume of all samples shows an obvious linear relationship with the pressure. The values of the constant N can thus be obtained by fitting the slopes of the linear relation as presented in Table 4. Then, based on Equation (7), it is possible to acquire the shale matrix compressibility for all samples. The calculated shale matrix compressibility is within the range of 0.23×10^{-4} to $22.03 \times 10^{-4} \text{ MPa}^{-1}$, which varies greatly with the buried depth.

Table 4. Calculation parameters of the shale matrix compressibility at different depths of Longmaxi Formation in the Ning228 well.

Sample No.	$R_{o,m}$ (%)	V_m (cm^3/g)	N ($\times 10^{-4}$)	PV ($\times 10^{-3}$, cm^3/g)	C_m ($\times 10^{-4}$, MPa^{-1})
N228-1	4.45	0.37	6.00	14.49	2.42
N228-13	4.10	0.36	4.00	11.10	0.23
N228-24	4.18	0.37	10.00	11.13	16.60
N228-35	4.40	0.37	7.00	10.92	8.48
N228-46	4.20	0.37	8.00	13.20	9.14
N228-57	4.38	0.36	7.00	11.27	8.28
N228-67	4.18	0.36	9.00	11.47	13.62
N228-78	4.60	0.37	5.00	10.46	3.57
N228-88	4.32	0.39	13.00	12.27	22.03
N228-100	4.60	0.38	5.00	10.82	3.14

Note: V_m —shale matrix volume; C_m —shale matrix compressibility; PV—pore volume.

The calculation results of the shale matrix compressibility indicate that in the pressure band from 8.66 to 37 MPa, the shale matrix has already started to produce a shrinkage phenomenon under the influence of pressure changes. Thus, matrix shrinkage is also bound to occur at pressures greater than 37 MPa. Therefore, it can be concluded that when the mercury injection pressure reaches 8.66 MPa or more, the shale produces a matrix shrinkage phenomenon in the mercury intrusion porosimetry. It makes the mercury intrusion volume greater than the original pore volume, causing the pore volume measured by mercury injection data to be larger than the actual original pore volume. Therefore, in order to guarantee the correctness of the experimental conclusions obtained later when considering pore structure as an influencing factor for correlation analysis, full-aperture pore data are needed in order to study the effect of pore structure on shale matrix compressibility. Based on previous research results and the quantitative analysis of the pore structure of shale samples above, we use low-temperature N_2 adsorption experimental data to quantitatively

characterize micropores and mesopores. Quantitative characterization of macropores is performed using MIP data. On this basis, the influence of the shale pore structure on matrix compressibility is investigated below.

3.5. Shale Brittleness and Lithofacies Characteristics

Based on the results of XRD test analysis of all samples, the mineral brittleness index of the shale in the Ning228 well in the Yanjin area ranges from 36.2% to 81%, with an average of 56.78% by combining with the Equation (9). The empirical brittleness index in North America is 40%, which indicates that the brittleness of Longmaxi Formation shale in the Ning228 well in the Yanjin area is better than that in North America. This implies that the Longmaxi Formation shale in the Yanjin area can form complex network fractures rapidly during fracturing operations, which is conducive to shale oil and gas development.

According to the three-terminal element method of shale formation lithofacies classification, ten groups of shale samples can be divided into clay siliceous mixed shale, clay calcareous mixed shale, clay shale, and siliceous shale as shown in Figure 9. Among them, clay siliceous mixed shale is more distributed, which is more common in the study area. It is mainly distributed in the middle and upper parts of the selected Longmaxi Formation section, with an average TOC content of 1.4%. The mineral composition of this shale lithofacies is dominated by clay minerals, ranging from 36.3% to 48.4%, followed by siliceous minerals (including quartz and feldspar), ranging from 33.3% to 46.5%, and carbonate minerals (including calcite and dolomite) being the lowest. The clay calcareous mixed shale is mainly distributed in the upper part of the selected Longmaxi Formation section, with less distribution in the region. The clay shale is mainly distributed in the middle and lower parts of the selected Longmaxi Formation section, with a high clay mineral content, averaging 55.43%. The siliceous shale is mainly distributed in the lower part of the selected Longmaxi Formation section, with a high siliceous mineral content and abundant organic matter. Based on the above characteristics of shale samples, it can be found that there is a positive correlation between siliceous content and TOC content, indicating that the main siliceous body is biogenic and the early depositional environment of the Longmaxi Formation shale in the Ning228 well may be a deep-water shelf at a high sea level.

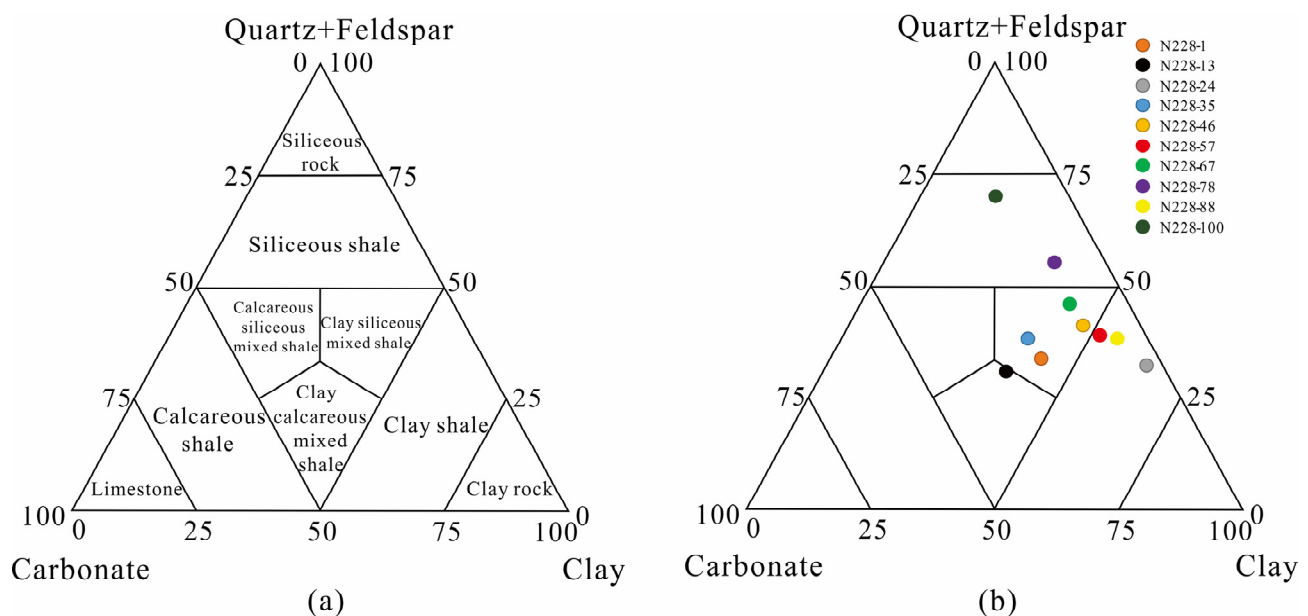


Figure 9. Lithofacies classification of Longmaxi Formation shale in the Ning228 well. (a) Three-terminal element method of shale formation lithofacies classification. (b) Lithofacies classification results for ten sets of shale samples.

4. Discussion

4.1. Effect of TOC on Shale Matrix Compressibility

Discarding the two excessive TOC anomalies, Figure 10 shows that the overall shale matrix compressibility is positively correlated with the increase of TOC content. We conclude that the effect of TOC in shale on the shale matrix compressibility can be regarded as a pore material filling problem. The high TOC content in shale enhances the softening effect of pore filling material on the shale skeleton, decreasing the overall shale modulus of elasticity and making the shale matrix susceptible to deformation due to pressure changes. Thus, it results in an increase in the shale matrix compressibility. Meanwhile, the high TOC content also indicates that the shale is rich in organic matter. Previous studies have shown that organic-rich shale often develops a large number of organic matter nanopores [50,51]. On the one hand, the rich organic matter provides a lot of space for the development of organic matter pores. On the other hand, the higher the organic matter content in the shale, the more organic acids and hydrocarbon gases will be generated during the maturation process, thus providing a large number of organic matter pores for the shale, which will lead to an increase in porosity and specific surface area. The rich pore space greatly enhances the compression effect of the shale matrix. Therefore, the effect of TOC on matrix compressibility mainly lies in the control of shale pore structure by organic matter.

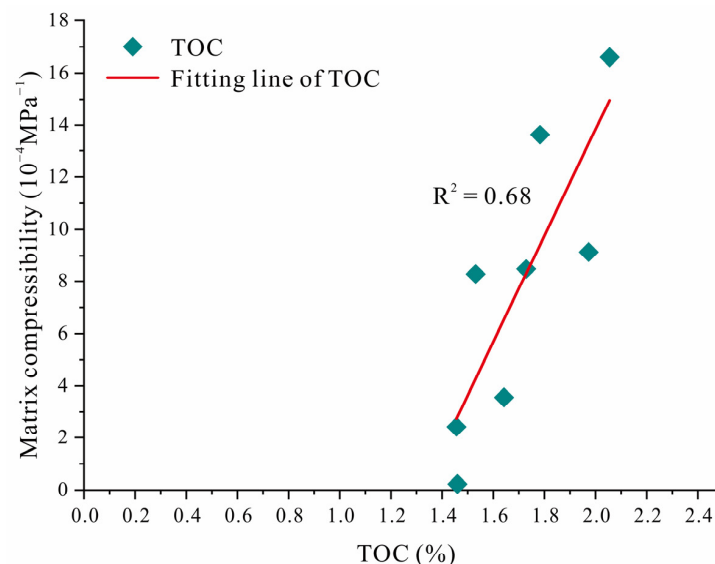


Figure 10. Relation between TOC content in shale and shale matrix compressibility.

4.2. Effect of Minerals on Shale Matrix Compressibility

As shown in Figure 11, the compressibility of the matrix is positively correlated with clay mineral content and negatively correlated with brittle mineral content and carbonate mineral content. These results agree with previous research that the higher the clay content, the stronger the corresponding shale stress sensitivity, causing the greater shale matrix compressibility. In addition, the relationship between shale lithofacies and matrix compressibility shows that clay shale and clay siliceous mixed shale with higher clay content tend to have higher matrix compressibility, while siliceous shale samples tend to correspond to lower matrix compressibility. It further validates the positive correlation between clay minerals and shale matrix compressibility. Meanwhile, previous studies have shown that clay minerals can be combined with organic matter to form organic clay complexes, in which a large number of organic matter pores are developed [50,52]. In the process of late diagenetic transformation, organic matter and clay mineral transformation promote each other, forming more intergranular pores of clay minerals. This will lead to the increase of porosity and specific surface area in shale and also affect its matrix compression characteristics. The role of minerals on the matrix compressibility of shale is also certainly

determined by various factors, such as whether the minerals fill the pore space, the state of mineral fugacity within the pore space, etc., which all influence the control effect of minerals on matrix compressibility.

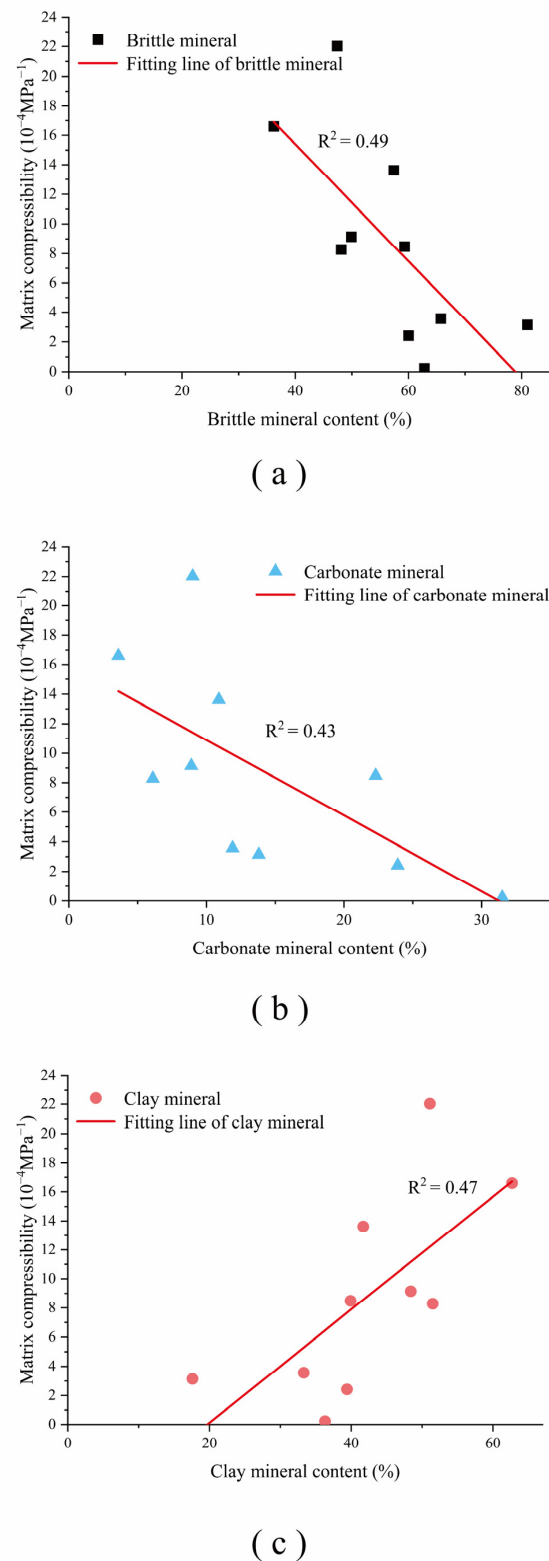


Figure 11. Relations between three types of mineral composition and shale matrix compressibility. (a) Brittle mineral and matrix compressibility. (b) Carbonate mineral and matrix compressibility. (c) Clay mineral and matrix compressibility.

4.3. Effect of Pore Structure on Shale Matrix Compressibility

The effect of pore structure on shale matrix compressibility is mainly reflected by porosity, specific surface area, total pore volume, and pore size in this work. Figure 12a shows that there is a positive correlation between shale matrix compressibility and porosity. The higher porosity of shale indicates that the matrix has more pore space. On the one hand, when the pressure increases, these pore spaces are more susceptible to compression. On the other hand, these empty pore spaces may be filled with organic matter or clay minerals, thus reducing the overall elastic modulus of shale and resulting in enhanced stress sensitivity of shale, which in turn leads to enhanced shale matrix compressibility. Figure 12b shows that the shale matrix compressibility overall has a more obvious positive correlation with specific surface area. The larger specific surface area indicates that the shale is more heterogeneous and the pore structure is more complex. This may imply that the shale with more complex pore structure has stronger matrix compressibility. The positive effect of specific surface area on shale matrix compressibility is stronger than porosity. Figure 12c shows a weak positive correlation between shale matrix compressibility and total pore volume. This means that specific surface area and porosity are the critical parameters that affect the compressibility of the deep marine shale matrix. Figure 12d indicates the effect of different pore sizes on matrix compressibility. The shale matrix compressibility has a significant positive correlation with micropore content, a positive correlation with mesopores, and no obvious relationship with macropore content. It can be synthesized to show that the pore content in shale has a positive effect on the matrix compressibility, especially the effect of micropore content. The larger micropore content in shale corresponds to larger porosity and specific surface area, indicating that the shale matrix is more easily compressed.

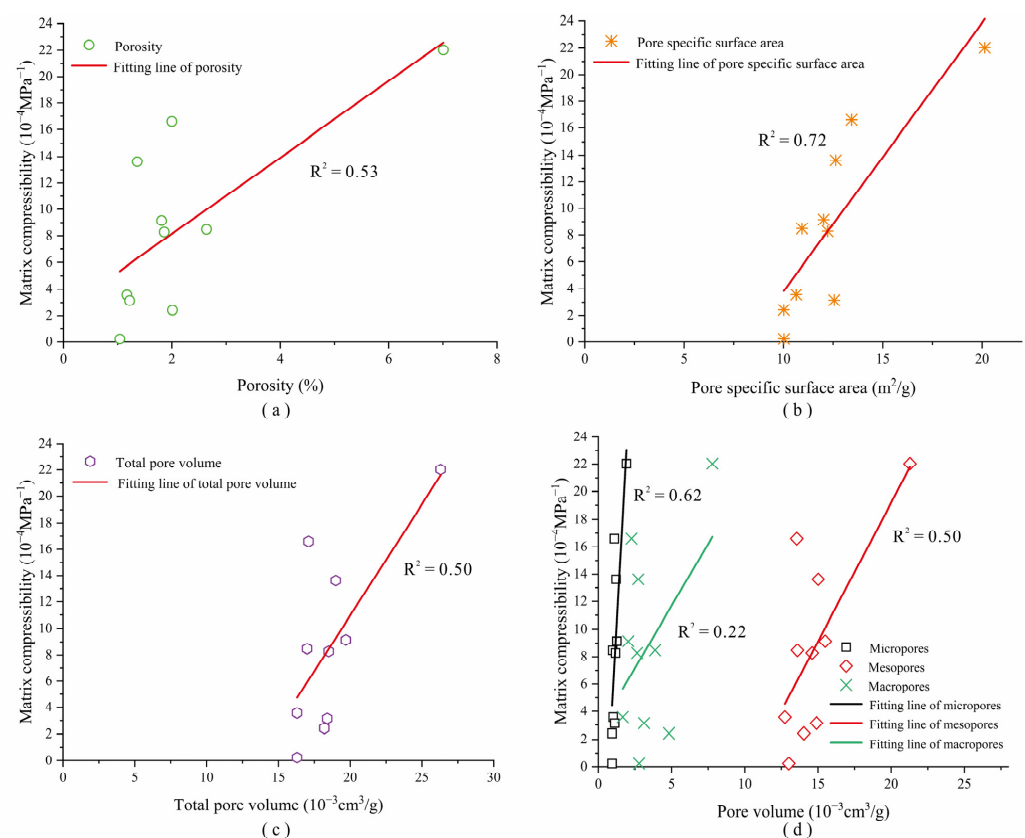


Figure 12. Relations between pore structure and shale matrix compressibility. (a) Porosity and matrix compressibility. (b) Total pore volume and matrix compressibility. (c) Specific surface area and matrix compressibility. (d) Pore size and matrix compressibility.

4.4. Relationship between Brittleness Index and Matrix Compressibility

Figure 13 shows that shale matrix compressibility is somewhat negatively correlated with the brittleness index. This indicates that with greater rock brittleness, the shale matrix is more resistant to volume compression caused by pressure change. Matrix compressibility is defined as the amount of change in matrix volume per unit mass sample at unit incremental pressure, which is an elastic deformation. As for oil and gas reservoirs, rock brittleness is generally defined as the ease of transient changes before rock fracture [53,54]. Macroscopically, the larger the brittleness index is, the easier it is for the rock to form fractures, making the microscopic rock matrix less susceptible to its internal compressibility. This view is consistent with our understanding of rock brittleness and matrix compressibility.

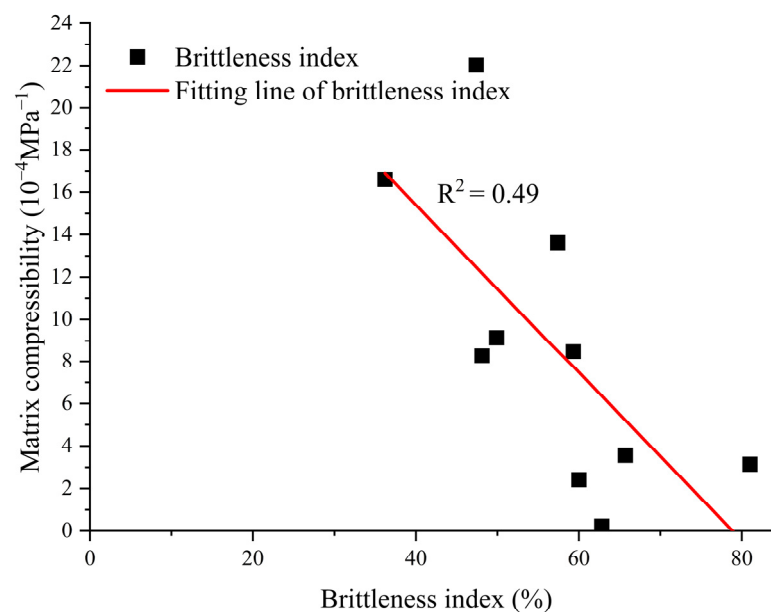


Figure 13. Relationship between brittleness index and shale matrix compressibility.

5. Conclusions

When applying the MIP combined with the low-temperature N_2 adsorption/desorption experiment to evaluate the pore structure of shale, it is necessary to consider the matrix volume compression changes caused by mercury intrusion into pore fissures. Factors that affect the shale matrix compressibility were also discussed herein. We determined that the matrix compressibility of shale from Ning228 in the Yanjin area varies in the range of 0.23×10^{-4} to $22.03 \times 10^{-4} \text{MPa}^{-1}$ as the buried depth changes. The following conclusions were drawn.

(1) The shale of the Ning228 well in the Yanjin area consists of all marine, over-mature, hydrocarbon source rocks, but it still maintains a certain degree of porosity. Its organic matter content is typically high in the lower section and low in the upper section, with increasing burial depth, which is mainly related to the depositional background of the Longmaxi Formation in the Yanjin area. Mesopores are the main components of shale pores in the Longmaxi Formation of the Ning228 well in the Yanjin area, which is the main occurrence site for shale gas.

(2) The average mineral brittleness index of Ning228 well shale in the Yanjin area is 56.78%, which implies that the Longmaxi Formation shale in the study area can form complex mesh fractures rapidly during fracturing operation. The shale here can be divided into clay siliceous mixed shale, clay calcareous mixed shale, clay shale, and siliceous shale. Among these, clay siliceous mixed shale is more distributed in the study area. The main siliceous body of the Longmaxi Formation shale in the Ning228 well is biogenic, indicating that its early depositional environment may be a deep-water shelf with high sea level.

(3) The shale matrix compressibility is positively correlated with the increase of TOC. The high TOC content in shale can enhance the softening effect of pore filling material on the shale skeleton, decreasing the overall shale modulus of elasticity and making the shale matrix susceptible to deformation due to pressure changes. The matrix compressibility is positively correlated with clay mineral content and negatively correlated with brittle mineral content and carbonate mineral content. The higher the clay mineral content, the stronger the corresponding shale stress sensitivity, causing greater shale matrix compressibility. The influence of TOC and minerals on the compressibility of the shale matrix is mainly reflected in the control effect on the pore structure.

(4) The pore structures of shale—including porosity, specific surface area, total pore volume, and pore size—are all positively correlated with matrix compressibility. The pore content in shale has a positive effect on the matrix compressibility, and the pore specific surface area is critical for effective changes in shale matrix compressibility, indicating that the complexity of shale pore structure is the key factor affecting matrix compressibility.

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