ACS OMEGA

http://pubs.acs.org/journal/acsodf

Article

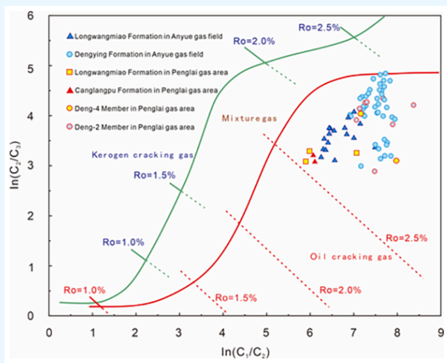
Geochemical Characteristics and Origin of Sinian-Cambrian Natural Gas in Penglai Gas Area, Sichuan Basin

Lu Zhang, Jian Li, Zengye Xie,* Jianying Guo, Aisheng Hao, Yifeng Wang, Nan Su, Jin Li, Zhisheng Li, Dawei Chen, and Dongxue Zhu

Cite This: *ACS Omega* 2024, 9, 23390−23399

Read Online

ABSTRACT: The Sichuan Basin in southern China is well-known for its large natural gas resource potential stored in Sinian-Cambrian systems. Recently, high-yield industrial gas flow has been discovered from the Dengying Formation (Sinian System) and Canglangpu Formation (Cambrian System) in the Penglai gas area, preluding the multilayer stereoscopic exploration in Sichuan Basin. However, the origin of the natural gas and its preserving mechanics is still debated, and thus, in this study the geochemical characteristics of the natural gas are systematically analyzed, based on the data from gas composition and hydrocarbon isotope of a series of local wells. On this basis, the geochemical characteristics of natural gas in different regions and layers are compared, and the reasons for these differences from the origin and influencing factors are analyzed. The results show the following: (1) The natural gas of the Penglai gas field is dry gas dominated by CH_4, and the Sinian Dengying Formation gas has lower C_2H_6 content, larger dryness coefficient, heavier $\delta^{13}C$, and lighter $\delta^{2}H_{CH4}$ than the Cambrian gas, which is associated with the high proportion of hydrocarbons from the high-maturity Dengying source rocks. (2) The natural gas from some wells in the lower part of the structure is characterized by high H_2S content and low CH_4 content, and heavy $\delta^{13}C$ in the components, which seems to be affected by the thermochemical sulfate reduction (TSR) effect. (3) The natural gas from the Penglai gas area has a relatively low maturity, which appears to be attributed to the continuous sealing ability of the caprock, which can preserve both the early generated gas and the late thermal-cracked gas.



1. INTRODUCTION

The Sichuan Basin in China is widely regarded as one of the largest natural gas bearing basins in China. The Anyue gas field, for example, is China's largest marine carbonate gas field, exceeding one trillion cubic meters of proven geological reserves by the end of 2020.[1] Similar to the Anyue gas field in the hydrocarbon source and geological structure condition, the Penglai gas area located at the northern slope of the central Sichuan paleo-uplift, likewise shows favorable exploration potential in the Sinian-Cambrian system,[2−4] and its hydrocarbon accumulation features are characterized as "three-dimensional hydrocarbon supply, three-dimensional reservoir formation, three-dimensional transportation, early oil and late gas, three-dimensional accumulation".[5−9] Recently, exploration breakthroughs have been achieved in this area, targeting the second and fourth members of the Dengying Formation (hereinafter referred to as Deng-2 Member and Deng-4 Member), the Canglangpu Formation, Xixiangchi Formation, as well as the Permian Maokou Formation,[5] broadening the exploration field of deep and ultradeep natural gas in the Sichuan Basin.

The geochemical characteristics are of great significance for the analysis of the origin, type, maturity, and reservoir formation process of natural gas. Natural gas is mainly composed of a few low molecular weight hydrocarbons, and its genesis analysis mainly relies on hydrocarbon isotopes and component content. Albeit the similarities in the reservoir forming conditions, there remain many significant differences in gas composition and isotope characteristics between this area and the widely studied and successfully developed Anyue gas field.[1,10−15] In addition, the geochemistry features vary with layers in this area, and to date, there is no general agreement about their genetic mechanism differences, including the difference in the proportion contribution of Sinian sources,[1,16] the source of crude oil cracking gas[17−22] and ultralate shale source gas,[23,24] and the influence of water participating in the reaction in the high evolution stage,[25−27] which constrained the understanding of the natural gas accumulation and reservoir formation processes of the two

Received: December 18, 2023
Revised: May 7, 2024
Accepted: May 13, 2024
Published: May 23, 2024

https://doi.org/10.1021/acsomega.3c10109
ACS Omega 2024, 9, 23390−23399

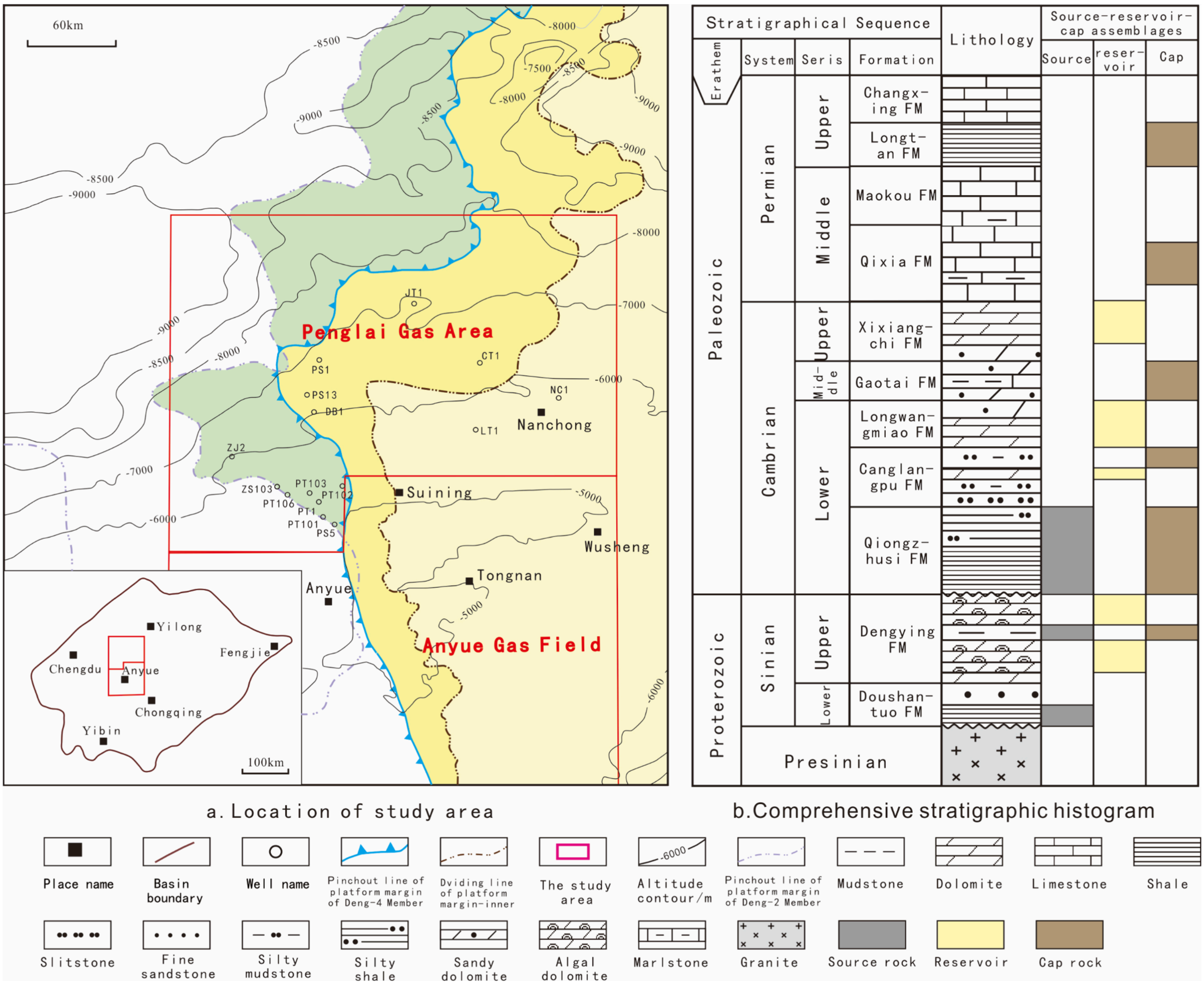


Figure 1. (a) Location of the study area and (b) the stratigraphic histogram. Panels a and b are adapted with permission from ref 5. Copyright 2022 Acta Petrolei Sinica.

areas. Therefore, this study investigates the geochemical characteristics such as composition and isotopes from the newly acquired wells in different layers of the Penglai gas area and attempts to explain the characteristics from its maturity, TSR reaction, and sealing performance of multiple overlying cap layers. This work aims to offer in-depth insights concerning the reservoir forming conditions and the exploration of deep natural gas reservoirs in the Sichuan Basin.

2. GEOLOGICAL SETTING

The Sichuan Basin is a continental basin located on the northwest side of the Yangtze Platform with abundant gas resources in the Sinian-Cambrian strata. The Sinian strata in this basin can be divided into Doushantuo (Z_1d) and Dengying (Z_2dn) Formations, and the latter can be further subdivided into Z_2dn^1, Z_2dn^2, Z_2dn^3, and Z_2dn^4 from the bottom up. The lower Cambrian system in this basin includes the Qiongzhusi (ϵ_1q), Changlangpu (ϵ_1c), and Longwangmiao (ϵ_1l) formations. The overlying strata are Middle Cambrian Gaotai (ϵ_2g) and Upper Cambrian Xixiangchi (ϵ_3x) formations (Figure 1). The Sichuan Basin has undergone multiple tectonic movements from basement formation to the formation of the orogenic basin.[5,28] In the Sinian-Cambrian period, 3 episodes of the Tongwan movement occurred in the Central Sichuan Basin, forming 2 ancient uplifts (i.e., the Gaoshiti-Moxi and Ziyang-Weiyuan uplifts) and one ancient rift (i.e., the Deyang-Anyue ancient rift).[29] Later, influenced by the Caledonian Movement, the scope of the central Sichuan paleo-uplift was further expanded. In the Indosinian, Yanshanian, and Himalayan periods, the basin shape was inherited, albeit with moderate adjustment and transformation, laying a good foundation for oil and gas accumulation in high parts. Before the late Indosinian period, the Penglai gas area and the Anyue gas field had similar tectonic backgrounds, both located in the high part of the structure;[5] however, in the late Indosinian-Himalayan period, the tectonic evolution of the two became distinct. Specifically, the Anyue gas field is in the high position of the structure permanently with weak structural deformation, while the Penglai gas area suffered from compression and subsidence, forming the monoclinic structure in the north of the present paleo-uplift (Figure 1).[5]

The tectonic framework of the uplift and depression alternation was formed in this basin during the Sinian period, which controls the development of the hydrocarbon generation

https://doi.org/10.1021/acsomega.3c10109
ACS Omega 2024, 9, 23390−23399

Table 1. Data Table of Sinian-Cambrian Natural Gas Components and Isotopes in Central Sichuan Basin

Well number	Depth (m)	Age	Main components (%)						C_1/C_{1+}	H_2S (g/m^3)	$\delta^{13}C$ (‰)		δ^2H (‰)	Refs
			CH_4	C_2H_6	CO_2	N_2	He	H_2S			CH_4	C_2H_6	CH_4	
NC1	5447	ϵ_3x	96.57	0.13	2.54	0.34	0.01	0.02	0.9987	0.36	−33.6	−32.5	−135	[1,30]
LT1	5337	ϵ_3x	91.81	0.10	7.56	0.20	0.01	0.01	0.9989	0.23	−34.1	−30.0	−126	
PS1	6588	ϵ_1l	69.74	0.07	27.41	0.67	0.01	2.10	0.9990	36.17	−34.1	−30.6	−138	this paper
DB1	5728	ϵ_1l	95.46	0.26	3.80	0.47	0	0.01	0.9973	0.30	−38.6	−39.1	−135	
PS13	6080	ϵ_1l	85.62	0.24	13.26	0.52	0.01	0.18	0.9972	5.19	−38.0	−39.2	−132	
JT1	6972	ϵ_1c	96.82	0.18	1.27	1.70	0.01	0.01	0.9981	0.14	−38.2	−36.4	−134	[1,30]
CT1	6264	ϵ_1c	94.13	0.21	5.00	0.38	0.01	0.04	0.9978	0.66	−35.8	−36.6	−136	
PS13	6655	Z_2dn^4	88.02	0.06	9.48	0.61	0.01	1.81	0.9993	14.87	−33.5	−28.4	−146	this paper
PS13	6655	Z_2dn^4	74.40	0.03	20.15	1.67	0.02	3.24	0.9996	54.93	−31.1	−27.5	−140	
PS1	7325	Z_2dn^4	23.03	0.02	59.47	1.62	0.02	15.75	0.9991	227.35	−29.3	−26.7	−144	
DB1	6537	Z_2dn^4	69.60	0.04	17.96	0.52	0.04	11.8	0.9994	211.02	−30.7	−26.3	−140	
PS5	5503	Z_2dn^4	84.21	0.03	12.94	0.60	0.01	2.14	0.9996	28.51	−34.3	−25.7	−141	
PS5	5775	Z_2dn^2	85.32	0.04	10.14	1.06	0.03	3.42	0.9995	46.78	−33.3	−28.0	−146	
PT1	5771	Z_2dn^2	92.83	0.07	4.42	0.56	0.01	2.11	0.9992	33.13	−34.7	−29.0	−140	[1,30]
PT101	5615	Z_2dn^2	90.95	0.07	5.89	0.55	0.01	2.52	0.9992	33.64	−34.6	−29.5	−141	
PT101	5855	Z_2dn^2	83.34	0.06	3.23	10.24	0.01	3.09	0.9993	39.00	−34.7	−29.0	−143	
PT102	5905	Z_2dn^2	89.88	0.06	5.25	0.80	0.02	3.71	0.9993	43.35	−34.4	−28.4	−137	
PT103	5725	Z_2dn^2	89.47	0.04	6.54	0.62	0.01	3.15	0.9996	37.46	−33.7	−29.1	−144	
ZJ2	6693	Z_2dn^2	79.20	0.04	15.43	0.67	0.05	4.50	0.9995	71.56	−35.1	−28.0	−141	
PT106	5750	Z_2dn^2	91.13	0.09	7.36	0.46	0.01	0.95	0.9990	20.11	−34.5	−30.3	−138	this paper
ZS103	6008	Z_2dn^2	90.23	0.02	5.94	0.73	0.02	3.06	0.9998	43.55	−33.4	−26.9	−144	
PS5	5775	Z_2dn^2	85.32	0.04	10.14	1.06	0.03	3.42	0.9995	46.78	−33.3	−28.0	−146	

center of source rocks and many sets of high-quality reservoirs for the central Sichuan Basin. The shape of the rift trough determines the thickness and distribution of the Lower Cambrian Qiongzhusi Formation, forming high-quality source rocks, which is the natural gas source for Sinian-Cambrian. The ϵ_1q and Z_2dn shales are considered major source rocks for petroleum in the Sinian-Cambrian strata.[19] The Ro value of Sinian source rocks in the basin is generally greater than 3.0%, and the Ro value of Cambrian source rocks is generally greater than 2.5%, both of which are in the high-over mature stage.[30]

Multiple sets of reservoirs are developed in the Penglai gas area. The reservoirs are vertically superimposed and horizontally connected, forming a Sinian-Cambrian multilayer stereoscopic reservoir. Controlled by the pattern of "platformal trough", the Dengying Formation in the Penglai gas area develops large-scale retrograde platform margin deposits,[2] and the mound-shoal complex is its favorable facies zone. The width of the platform edge of the Deng-2 Member is 40−130km, and the thickness is 650−1000m. The width of the Deng-4 Member is 20−70 km, and the thickness is 350−450 m.[7] Compared with the Anyue gas area, the width, thickness, and beach scale of the platform margin in the Penglai gas area are larger. On this basis, during the Tongwan movement, the Dengying Formation was uplifted twice to expose the sea surface, and the weathering leaching zone was formed on the surface of the Deng-2 Member and Deng-4 Member, so the reservoir was reformed.[5] The main sedimentary environments of the Canglangpu Formation and Longwangmiao Formation are shallow shelf and restricted platform, respectively, and the granular beach is a favorable facies zone for the development of high-quality reservoirs in these two layers. Similar to the Dengying Formation, the Cambrian reservoirs in the Penglai gas field, are also controlled by the comprehensive effect of "sedimentary facies + karstification",[5] which provides a strong reservoir foundation for the formation of large gas fields.

The Sinian-Cambrian gas reservoirs in the northern slope mainly develop 5 sets of reservoir and direct cap assemblages: (1) Deng-2 Member dolomite & Deng-3 Member shale; (2) Deng-4 Member dolomite & Qiongzhusi Formation shale; (3) Canglangpu Formation dolomite and sand-mudstone; (4) Longwangmiao Formation dolomite & Gaotai Formation dolomite-mudstone; (5) Xixiangchi Formation dolomite and middle Permian limestone (Figure 1). The widely distributed Upper Permian mudstone deposits also provide favorable regional preservation conditions for the underlying gas reservoirs. Furthermore, the interbank compact sediments in the updip direction of the slope and the cap rock together sealed the scale mound beach body, which is the key factor for the preservation of the Dengying Formation gas reservoir.

3. MATERIAL AND METHODS

Natural gas samples were collected at the wellhead using pressure resistant steel cylinders. The conventional geochemical analyses, including gas components, carbon isotopes, and hydrogen isotopes, were done at the Laboratory of Gas Reservoir Formation and Development, CNPC, on the Sinian-Cambrian representative natural gas samples from the wells in the Penglai gas area. Agilent 7890A gas chromatograph was used for routine analysis of natural gas components and C_1−C_3 composition analysis by large injection volume.[9,16] The carbon isotope composition of natural gas was performed by the Finnigan Delta PLUS XL GC/C/IRMS, with the carbon isotope composition of trace ethane enriched by liquid nitrogen freezing.[9,16] The hydrogen isotope composition was detected by the Finnigan Mat 253.[9,16]

According to the caprock lithology of the Sinian-Cambrian reservoirs in the Penglai gas area, 5 representative lithology

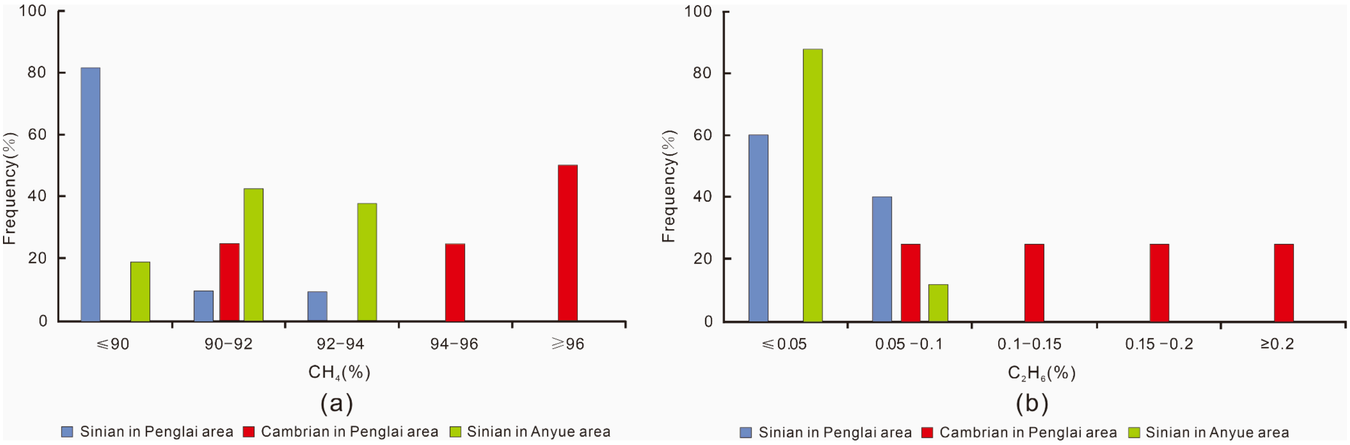


Figure 2. Histogram of methane and ethane content distribution in the central Sichuan Basin.

combinations were selected to conduct the high temperature and high-pressure rock breakthrough pressure test to compare their sealing performance. The test was conducted at room temperature. For the step pressurization breakthrough test, the pressure is repeatedly maintained for a specific time and then the pressure is increased until the gas breaks through.[31] For the constant pressure test, a constant pressure of 14 MPa was maintained until the gas broke through the rock sample.

4. RESULTS

4.1. Natural Gas Composition. Natural gas is primarily composed of saturated light paraffins; among them, CH_4 is usually dominant in the Sinian-Cambrian natural gas in the Penglai gas area (Table 1, Figure 2), albeit with varying proportions in the strata. After normalizing the hydrocarbon composition, the drying coefficient of all samples is greater than 0.9972 showing the strata contains the gas feature of dry gas. Specifically, the CH_4 content in Deng-2 Member, Deng-4 Member, and the Cambrian natural gas is in the ranges of 79.2%−92.83%, 23.03%−88.02%, and 69.74%−96.82%, respectively.

C_2H_6 is another hydrocarbon gas that exists in all samples, whose content is significantly lower than that of CH_4. Specifically, the proportion of C_2H_6 in Deng-2 Member, Deng-4 Member, and the Cambrian natural gas lies in 0.04%−0.09%, 0.02%−0.06%, and 0.10%−0.26%, respectively. There are also certain nonhydrocarbon gases existing in the studied samples, including CO_2, H_2S, N_2, He, and H_2, of which H_2S and CO_2 are dominant. The CO_2 and H_2S in the Deng-2 Member samples account for 3.23%−15.43% and 0.95%−4.5%, respectively, with the maximum values lower than the Deng-4 Member (9.48%−59.47% for CO_2, and 1.81%−15.75% for H_2S). And the corresponding values for the Cambrian natural gas are 1.27%−27.41% and 0.01%−2.1%, respectively. The Sinian Dengying Formation bears the highest content ranging from 14.87 to 227.35 g/m^3, which is followed by the Cambrian Longwangmiao Formation ranging from 0.3 to 36.17 g/m^3, and then the Cambrian Canglangpu Formation (0.14−0.66 g/m^3) and Xixiangchi Formation (0.23−0.36 g/m^3).

Regarding N_2 and He, both the Deng-2 and Deng-4 Members bear the proportions of 0.46%−10.24% and 0.01%−0.05%, respectively, and the corresponding values in Cambrian are 0.20%−1.70% and 0−0.01%, respectively.

4.2. Carbon and Hydrogen Isotope. The carbon and hydrogen isotopes of the methane are important parameters related to the condition of the aqueous medium and the degree of thermal evolution of source rocks.[1] Most $\delta^{13}C_1$ of natural gas from the Sinian and Cambrian systems in the Penglai gas area is lighter than −33‰. The average $\delta^{13}C_1$ values for the studied samples show a decreasing trend in the sequence from Deng-4 Fm., Deng-2 Fm., Xixiangchi Fm., Canglangpu Fm., to Longwangmiao Fm. (Figure 3). δ^2H_{CH4} of natural gas is −144%−137% in the Deng-2 Member, −146%−140% in the Deng-4 Member, and −136%−126% in the Cambrian system.

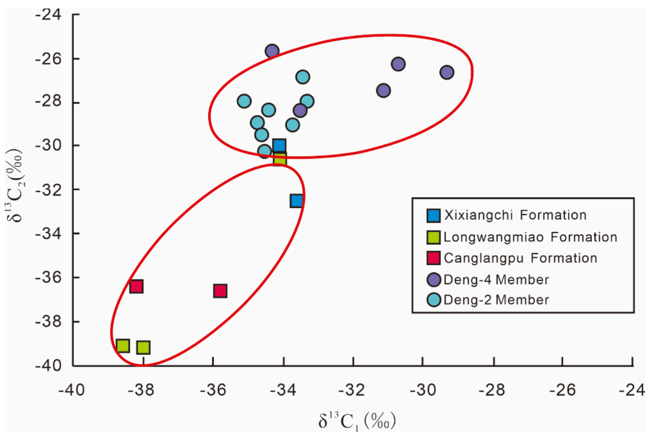


Figure 3. Carbon isotope frequency distribution histogram of methane and ethane in the central Sichuan Basin.

4.3. Breakthrough Pressure. The breakthrough pressure varies with the lithology combination (Figure 4). The tight dolomite first reached the breakthrough pressure of 3.5 MPa after 24 min, while the marlstone and shale recorded the breakthrough pressure and time of 3.5 MPa after 56 min and 6.5 MPa after 56 min, respectively. In comparison, the lithology combination of tight dolomite + dolomite + marlstone holds a higher breakthrough pressure (14 MPa) and longer duration time (2281 min). The combination of tight dolomite + dolomite + marlstone + semsle seems to bear the best sealing ability, which was not broken through in 14 days at 14 MPa.

https://doi.org/10.1021/acsomega.3c10109
ACS Omega 2024, 9, 23390−23399

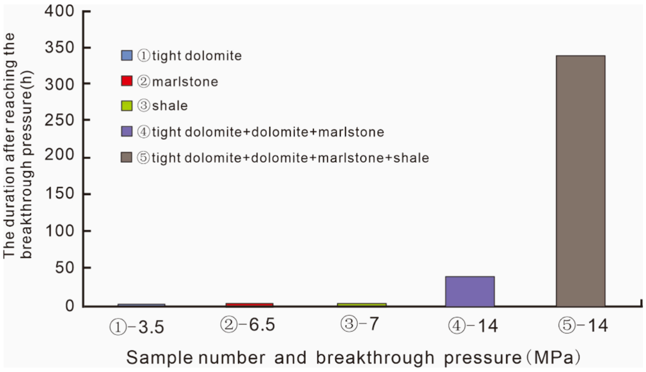


Figure 4. Breakthrough pressure and time of different samples. Note: Samples ①–③ adopt the conventional test method. Since the experimental confining pressure should follow the increase of gas pressure, to avoid the sample being crushed, samples ④ and ⑤ adopt the constant pressure method. The lithology combination is arranged from the bottom to the top.

5. DISCUSSIONS

5.1. Natural Gas Type. The classification of natural gas is crucial for assessing its sources and exploration potential, and the covariation of $\ln(C_1/C_2)$ and $\ln(C_2/C_3)$ diagram is a widely used approach to identifying the types.[32] According to Figure 5, for the Sinian-Cambrian natural gas samples in the Penglai gas area, all the samples belong to oil-cracking gas with $R_o > 2.5\%$, same as the Anyue gas field.[33] It is pointed out that the source rocks of the Sinian-Cambrian source rocks entered the overmature evolution stage in the Middle Jurassic, and then reached the maturity peak in the Cretaceous, during which period the crude oil massively cracked and generated substantial amounts of natural gas.[1] Besides the distinguishing plate, the existence of a large amount of reservoir bitumen under the reflected polarized light microscope (Figure 6) also suggests the occurrence of oil cracking.[33−35] It has been reported that the bitumen contents in the reservoirs of the Deng-2 Member, Canglangpu Formation, and Longwangmiao Formation can reach 4.7%, 1.9%, and 2.1%, respectively,[1] proving the development of paleo-oil reservoir with favorable gas generation capacity in the Penglai gas area.

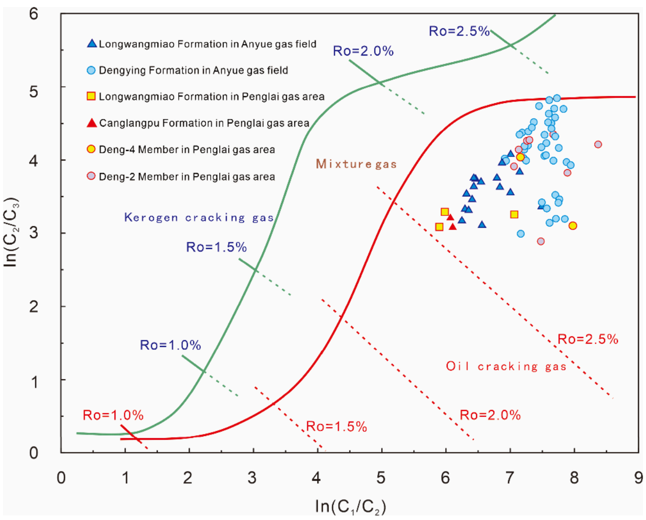


Figure 5. Identification of genetic types of natural gas from the Sinian Cambrian in the Penglai gas region (the data for the Anyue area comes from ref 1, 9, and 19). Adapted with permission from ref 32. Copyright 2016 Elsevier.

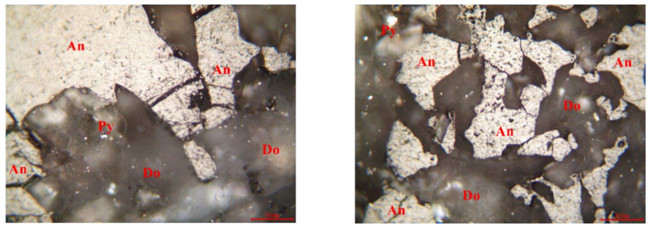


Figure 6. Asphalt photos in Sinian-Cambrian reservoirs in the Penglai gas area. Do, dolomite; An, bitumen; Py, pyrite.

5.2. Effect of Maturity and Water Salinity on Gas Composition. The gas geochemical features vary with formations, as shown in Figure 2, which signifies the various processes of natural gas accumulation. After eliminating the interference from nonhydrocarbon gases, the normalized dry coefficient (C_1/C_{1+}) exhibits a decreasing trend from the Deng-2 Member (0.9990−0.9998), to the Deng-4 Member (0.9990−0.9996), and then to the Cambrian system (0.9970−0.9990) (Table 1). In this area, the Cambrian source rock seems to be one of the main gas sources for the Dengying Formation and the Qiongzhusi Formation.[36] Meanwhile, the underlying old strata, the Sinian source rocks provide gases to the Dengying Formation, leading to a higher maturity of the natural gas in the Deng-2 and Deng-4 Members.[16,36−38] Owing to the high maturity, the content of CH_4 originating from the Sinian source rocks increases, and correspondingly, the content of heavy hydrocarbon components decreases like C_2H_6.

Thermal maturity not only affects the relative proportions of different hydrocarbon components but changes the values of $\delta^{13}C_1$ which tends to rise with depth, except for the Xixiangchi Formation bearing the gases from the Permian hydrocarbon source (Table 1). Also, maturity could increase the $\delta^{13}C_2$ values of the natural gas with a more obvious range.[39,40] Li et al. (2016) carried outgas generation experiments by thermal simulation on sapropelic source rocks and found that as the temperature increases to the maximum, the weight change amplitude of $\delta^{13}C_2$ was significantly greater than that of $\delta^{13}C_1$ (11.7% vs 5%), leading to the increase in $\Delta^{13}C_{2-1}$. Therefore, $\Delta^{13}C_{2-1}$ of the Sinian-Cambrian natural gas shows a significant correlation with the dry coefficient (Figure 7). Regarding the Dengying reservoir with mixed gas sources, the larger the contribution of Sinian source rocks, the heavier the $\delta^{13}C_2$ and the greater the $\Delta^{13}C_{2-1}$.

The change of δ^2H_{CH4} in natural gas is related to many factors, such as the thermal evolution degree of source rock, the type of organic matter, and the salinity of water in the sedimentary environment of source rock.[9,26] In this case, the natural gases of different formations are generated by in situ cracking of ancient gases formed by sapropelic hydrocarbon sources, and thus, the organic matter types may not be the major controlling factor. Regarding the effect of thermal evolution and salinity, both of them can lead to a heavy δ^2H_{CH4}.[41−44] However, the δ^2H_{CH4} of the Sinian natural gas is lighter than that of the Cambrian, suggesting maturity is also not the dominating factor influencing the isotopic variation, which means that salinity might be the principal controlling factor. The salinity of the ancient water medium in the sedimentary environment of the Cambrian Qiongzhusi Formation source rock is 18.5%,[45] which is higher than that of the Sinian source rock (about 7.5%−7.7%),[45] resulting in

https://doi.org/10.1021/acsomega.3c10109
ACS Omega 2024, 9, 23390−23399

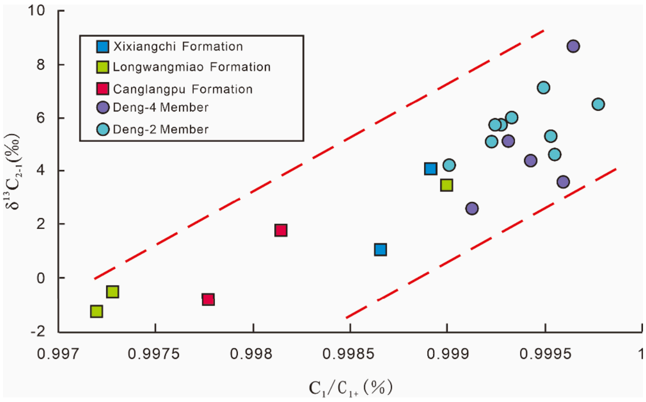


Figure 7. Relationship between the humidity coefficient and carbon isotope difference of methane and ethane in the central Sichuan Basin.

heavier δ^2H_{CH4} of natural gas. Because the Sinian natural gas is mixed sources of Sinian and Cambrian, while the Cambrian natural gas is only from the petroleum-cracking of the Cambrian, the Cambrian natural gas is more obviously affected by the high-salinity source rocks and thus has heavier δ^2H_{CH4}.

5.3. Effect of Thermochemical Sulfate Reduction (TSR). H_2S is a common component of oil and gas production, reaching concentrations up to over 4% in the Penglai gas region, far exceeding other strata (Figure 8). It is normally accepted that thermochemical sulfate reduction (TSR) is the most important process to generate abundant H_2S in carbonate gas reservoirs.[46] This redox reaction occurs between oxidative sulfates and reductive hydrocarbons, generating CO_2, H_2S, organic sulfur compounds, and/or diamondoids. In addition to the high H_2S content, the generated natural gas also has a high dryness coefficient, and heavy $\delta^{13}C_2$. During the TSR reaction, the ^{13}C-poor C_2H_6 will be preferentially consumed, thus the carbon isotope of residual C_2H_6 in natural gas gradually becomes heavier.[47] In the studied case, some natural gas from the Dengying Formation with a depth exceeding 6000 m in the Penglai gas area has abnormally heavy $\delta^{13}C_2$ carbon isotopes, such as Well DB1 and Well PS1, reaching −26.28% and −26.7%, respectively, heavier than that of the corresponding kerogen (Figure 9, Figure 10). The results seem counter-intuitive since normally the $\delta^{13}C_2$ of natural gas is lighter than that of kerogen. Therefore, it is supposed the heavy carbon isotope in the natural gas is not entirely caused by the difference of source rocks, but TSR reaction may be the main causer of this phenomenon in this area. Furthermore, the TSR reaction will affect the coke structure of the reservoir asphalt, which will lead to the isotropic-fine-grained mosaic structure of the coke asphalt.[48] The distribution of the fine-grained mosaic structures wrapped in fibrous structures in the reservoir asphalt of Well PT1[47] also proves the existence of a TSR reaction.

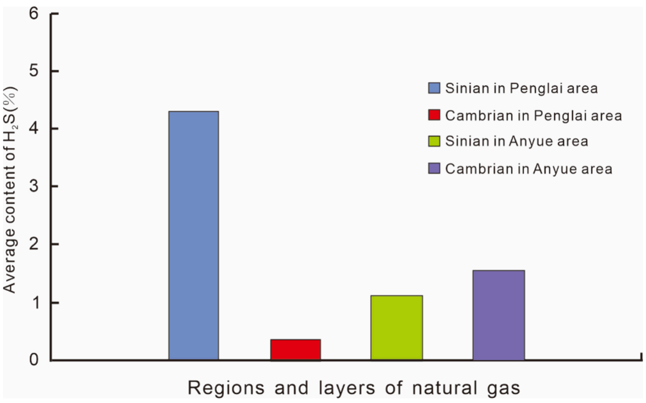


Figure 8. H_2S content in Sinian-Cambrian natural gas in Penglai and Anyue gas areas. Further evidence of the TSR effect comes from the carbon isotope.

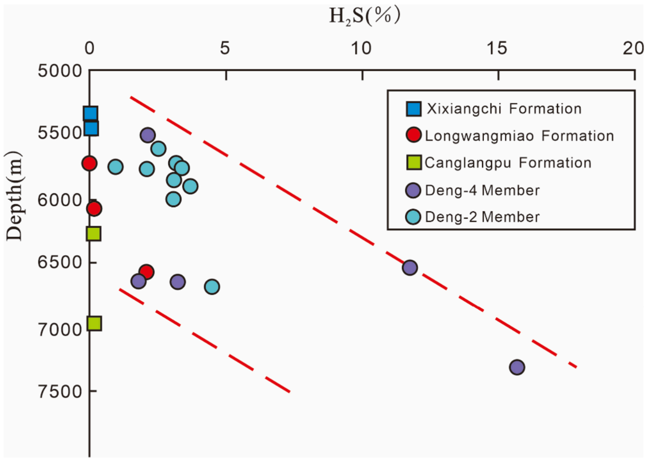


Figure 9. Relationship between H_2S content of natural gas and burial depth in the Dengying Formation and Cambrian in the central Sichuan Basin.

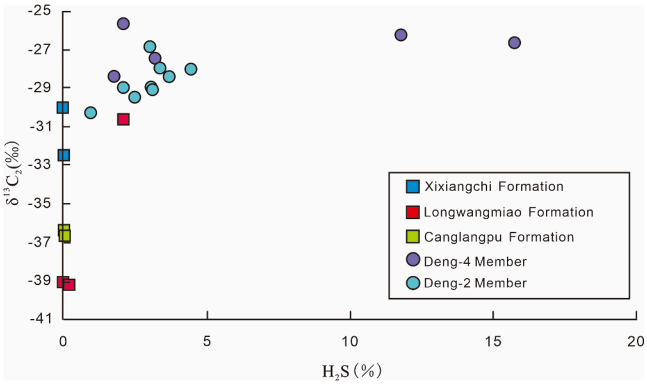


Figure 10. Relationship between H_2S content and $\delta^{13}C_2$ of natural gas in the Dengying Formation and Cambrian in the central Sichuan Basin.

Generally, the rate of hydrocarbon TSR reaction can be accelerated by higher temperature.[49,50] The H_2S content in natural gas directly from source rocks or crude oil is usually less than 3%.[26,51,52] In the studied region, the samples in wells buried deeper are more obviously influenced by hydrothermal activities, thus bearing an H_2S content of more than 10%, larger than other wells (<3%). Laterally, the Dengying Formation in the Penglai gas area is deeper than that in the Anyue gas area, thus maintaining a higher H_2S content in the Penglai gas area.

5.4. Preservation Conditions. Preservation condition is also a key factor deciding the natural gas components, and generally better preservation could result in a lighter $\delta^{13}C_1$ of natural gas because the early generated light gas components tend to be better preserved. In the Penglai gas area, Deng-2 Members in Well PT1, PT101, PT103, and PT106 are buried between 5600 and 5900 m, and their natural gas bears $\delta^{13}C_1$ as −34.7%, −34.6%, −33.7%, and −34.5%, respectively. The

https://doi.org/10.1021/acsomega.3c10109
ACS Omega 2024, 9, 23390−23399

buried depth of Deng-2 Member in Well ZJ2 is more than 6600 m with a $\delta^{13}C_1$ around −35.1%. By contrast, in the Gaoshiti-Moxi area of the Anyue gas field, the $\delta^{13}C_1$ of the Deng-2 Member of Well GS1, GS11, MX8, and MX17 are −32.3%, −33.3%, −32.8%, and −33.3%, respectively,[9] generally heavier than that of the Penglai gas area, and the formation depths are between 5100 and 5500 m, shallower than their counterpart in the Penglai gas area.

In general, the $\delta^{13}C$ of natural gas generated from the sapropelic kerogen becomes heavier with thermal evolution, and thus the deep reservoirs tend to maintain heavier $\delta^{13}C$ as they may experience higher thermal pressure. However, in the Penglai gas area, the gas from the Deng-2 Member is 1000 m deeper than that in the Anyue gas field but with lighter $\delta^{13}C_1$, which is contrary to the conventional understanding. According to gas cracking simulation experiments, the $\delta^{13}C$ of gas generated in the late stage is heavier than the $\delta^{13}C$ of crude oil (Figure 11). Here, it is speculated that the lighter carbon isotope in the Penglai gas area is related to the natural gas storage stage; i.e., the gas reservoir in the Penglai gas area captured almost all the generated gas including the early formed lighter gas and the later formed heavier gas, and thus its gas isotope results from the mixing gas characteristics. This incredibly favorable gas preservation benefits from the multiple tight overlying layers spreading the large proportion of the Sichuan Basin. While for the Anyue gas field, albeit the favorable caprocks, its bottom directly contacts with the permeable layers which causes the escape of the early generated gas from the reservoir bottom under the increasing pressure from the accumulation of the late generated gas. The loss of the isotopically lighter gas generated earlier increase the total gas isotope values measured with the mixing gas currently stored in the reservoir.[53] Thus, the $\delta^{13}C_1$ is lighter, and the proportion of early cracking gas is smaller, the $\delta^{13}C_1$ is heavier.

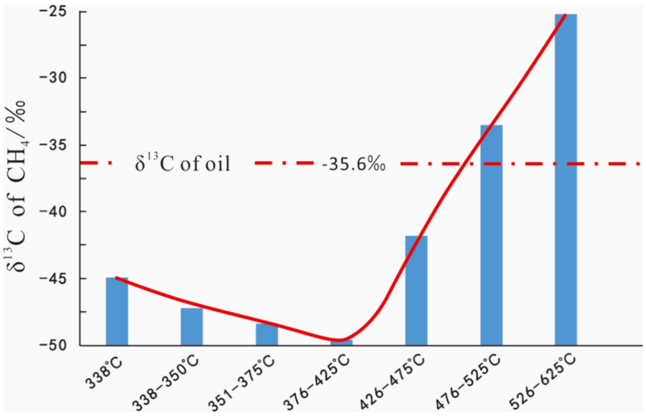


Figure 11. Hydrocarbon gas yield and methane isotope characteristics of crude oil cracking

The breakthrough pressure of the caprocks could effectively indicate the sealing ability of the caprocks. According to the evaluation experiment of the sealing ability of multistage caprock (Figure 4), when there are dense layers inside the gas reservoir (multiple sets of reservoirs) and multiple sets of caprocks above, the breakthrough pressure of caprock increases obviously, and the speed of gas breakthrough slows down. The study of deep gas accumulation in the Sichuan Basin indicates that the cumulative diffusion amount calculated by the diffusion model of multilayer caprock is significantly lower than that calculated by the single caprock.[54] These together mean that the stacking of multiple sets of caprocks overlying a gas reservoir can have a better blocking effect on the escape of natural gas. In the Penglai gas area, because there are many sets of caprocks such as tight dolomite in the Dengying Formation, shale in the Cambrian Qiongzhusi Formation, and Permian Longtan Formation above the Sinian gas reservoir (Figure 1), the natural gas is well preserved. Based on the rock physical characteristics reflected by logging data,[55,56] combined with the burial history analysis of the caprock, the history of the breakthrough pressure evolution can be obtained. According to the results, several sets of caprocks had possessed sealing ability since the early stage of crude oil cracking[1] (Figure 12), and thus present the current geochemical characteristics. Therefore, owing to the favorable preservation condition, the Sinian gas reservoir in the Penglai gas area sealed the gas from the early to late stages of crude oil cracking, and retained the difference in the geochemical characteristics of Sinian-Cambrian natural gas.

6. CONCLUSIONS

(1) Both Sinian and Cambrian natural gas in the Penglai gas field belong to dry gas, which was originated from the cracking of crude oil, although they have different gas sources and geochemical characteristics. The natural gas of the Sinian Dengying Formation has relatively lower C_2H_6 content, higher drying coefficient, heavier $\delta^{13}C$, and lighter δ^2H_{CH4}, compared with the natural gas of the Cambrian system.

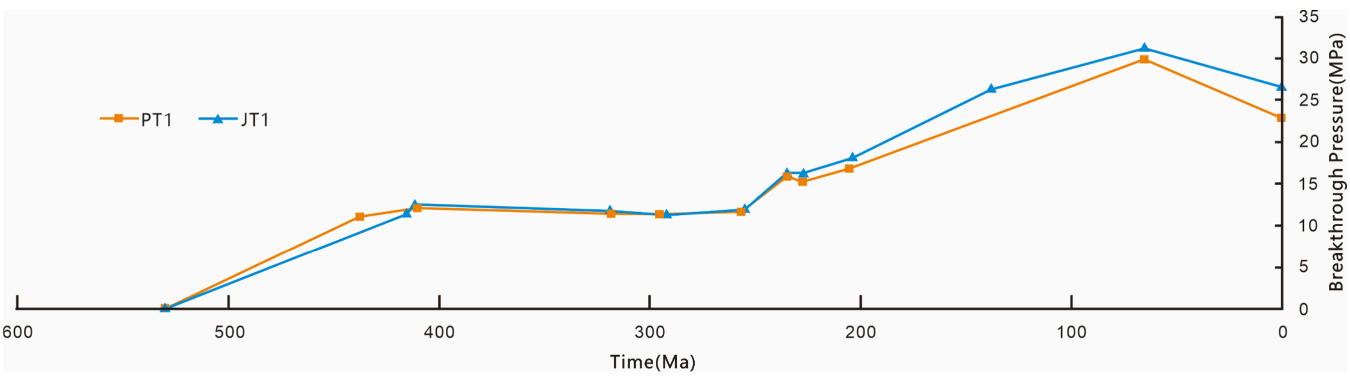


Figure 12. Evolution of the breakthrough pressure of caprock of the Qiongzhusi Formation in different periods.

https://doi.org/10.1021/acsomega.3c10109
ACS Omega 2024, 9, 23390−23399

(2) The natural gas of Dengying Formation in some low structural areas of the Penglai gas area is more significantly affected by the TSR reaction, showing higher sulfur content, resulting in a low methane content in the components and heavier δ^{13}C.

(3) The continuous sealing ability of the caprock and the overlapping sealing of multiple caprocks provide good preservation conditions for the Dengying Formation in the Penglai gas area, preserving both the early generated gas and the late thermal-cracked gas, thus showing a relatively low maturity.

AUTHOR INFORMATION

Corresponding Author

Zengye Xie − *PetroChina Research Institute of Petroleum Exploration & Development, Beijing 100083, China; Key Laboratory of Gas Reservoir Formation and Development, CNPC, Langfang 065007, China*; Email: xiezengye69@petrochina.com.cn

Authors

Lu Zhang − *PetroChina Research Institute of Petroleum Exploration & Development, Beijing 100083, China; Key Laboratory of Gas Reservoir Formation and Development, CNPC, Langfang 065007, China; PetroChina Shenzhen New Energy Research Institute Co., Ltd., Shenzhen 518000, China*; orcid.org/0009-0005-3802-9428

Jian Li − *PetroChina Research Institute of Petroleum Exploration & Development, Beijing 100083, China; Key Laboratory of Gas Reservoir Formation and Development, CNPC, Langfang 065007, China*

Jianying Guo − *PetroChina Research Institute of Petroleum Exploration & Development, Beijing 100083, China; Key Laboratory of Gas Reservoir Formation and Development, CNPC, Langfang 065007, China*

Aisheng Hao − *PetroChina Research Institute of Petroleum Exploration & Development, Beijing 100083, China; Key Laboratory of Gas Reservoir Formation and Development, CNPC, Langfang 065007, China*

Yifeng Wang − *PetroChina Research Institute of Petroleum Exploration & Development, Beijing 100083, China; Key Laboratory of Gas Reservoir Formation and Development, CNPC, Langfang 065007, China*

Nan Su − *PetroChina Research Institute of Petroleum Exploration & Development, Beijing 100083, China*

Jin Li − *PetroChina Research Institute of Petroleum Exploration & Development, Beijing 100083, China; Key Laboratory of Gas Reservoir Formation and Development, CNPC, Langfang 065007, China*

Zhisheng Li − *PetroChina Research Institute of Petroleum Exploration & Development, Beijing 100083, China; Key Laboratory of Gas Reservoir Formation and Development, CNPC, Langfang 065007, China*

Dawei Chen − *PetroChina Research Institute of Petroleum Exploration & Development, Beijing 100083, China*

Dongxue Zhu − *PetroChina Shenzhen New Energy Research Institute Co., Ltd., Shenzhen 518000, China*

Complete contact information is available at:
https://pubs.acs.org/10.1021/acsomega.3c10109

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors would like to acknowledge the Science and Technology Project of CNPC (Grant No. 2021DJ0604).

REFERENCES

(1) Wei, G. Q.; Xie, Z. Y.; Yang, Y.; Li, J.; Yang, W.; Zhao, L. Z.; Yang, C. L.; Zhang, L.; Xie, W. R.; Jiang, H.; et al. Formation conditions of Sinian-Cambrian large lithologic gas reservoirs in the north slope area of central Sichuan Basin, SW China. *Petroleum Explor. Dev.* **2022**, *49*, 963−976.

(2) Ma, K.; Wen, L.; Zhang, B. J.; Li, Y.; Zhong, J. Y.; Wang, Y. L.; Peng, H. L.; Zhang, X. H.; Yan, W.; Ding, Y.; et al. Segmented evolution of Deyang-Anyue erosion riftt rough in Sichuan Basin and its significance for oil and gas exploration, SW China. *Petroleum Explor. Dev.* **2022**, *49*, 313−326.

(3) Yang, Y. M.; Wen, L.; Luo, B.; Wang, W. Z.; Shan, S. J. Hydrocarbon accumulation of Sinian natural gas reservoirs, Leshan-Longnüsi paleohigh, Sichuan Basin, SW China. *Petroleum Explor. Dev.* **2016**, *43*, 197−207.

(4) Yue, H.; Zhao, L. Z.; Yang, Y.; Xie, J. R.; Wen, L.; Luo, B.; He, Y.; Chen, Y. L.; Wang, W. Z. Great discovery of oil and gas exploration in Cambrian Canglangpu Formation of the Sichuan Basin and its implications. *Natural Gas Industry* **2020**, *40*, 11−19.

(5) Yang, Y.; Wen, L.; Song, Z. Z.; Zhang, B. J.; Yan, W.; Zhou, G.; Tian, X. W.; Zhong, Y.; He, Y.; Ma, K.; Li, K. Y.; Yang, D. L.; Sun, Y. T.; Ge, B. F.; Yang, Z. Z. Breakthrough and potential of natural gas exploration in the multi-layer system of Penlai gas area in the north of central Sichuan paleo-uplift. *Acta Petrolei Sinica* **2022**, *43*, 1351−1368.

(6) Ma, K.; Zhang, X. H.; Peng, H. L.; Sun, Y. T.; Yang, D. L.; Tian, X. W.; Zhong, J. Y.; L, W. Y. Tectonic evolution of Moxi north slope in Sichuan Basin and its effect on forming Sinian oil and gas reservoirs. *Natural Gas Exploration and Development* **2020**, *43*, 8−15.

(7) Xu, C. C.; Shen, P.; Yang, Y. M.; Zhao, L. Z.; Luo, B.; Wen, L.; Chen, K.; Ran, Q.; Zhong, Y.; Peng, H. L. New understandings and potential of Sinian-lower Paleozoic natural gas exploration in the central Sichuan paleo-uplift of the Sichuan Basin. *Natural Gas Industry B* **2021**, *8*, 105−113.

(8) Song, Z. Z.; Liu, G. D.; Luo, B.; Zeng, Q. C.; Tian, X. W.; Dai, X.; Jiang, R.; Wang, Y. L.; Li, Q.; Zhao, J. Y.; et al. Logging evaluation of solid bitumen in tight carbonate in deep-buried and ultradeep-buried strata of the central Sichuan Basin. *Acta Sedimentologica Sinica* **2021**, *39*, 197−211.

(9) Xie, Z. Y.; Li, J.; Yang, C. L.; Tian, X. W.; Zhang, L.; Li, J.; Li, Z. S.; Guo, J. Y.; Xie, W. R.; Guo, Z. Q.; et al. Geochemical characteristics of Sinian-Cambrian natural gas in central Sichuan paleo-uplift and explration potential of Taihe gas area. *Natural Gas Industry* **2021**, *41*, 1−14.

(10) Zhang, L.; Xie, Z. Y.; Wang, Z. H.; Zhan, M. W.; Guo, J. Y.; Li, Y. H. Caprock characteristics and sealing ability evaluation of Sinian-Cambrian gas reservoirs in Gaoshiti-Moxi area, Sichuan Basin. *Natural Gas Geoscience* **2015**, *26*, 796−804.

(11) Lu, X. S.; Liu, S. B.; Tian, H.; Ma, X. Z.; Yu, Z. C.; Fan, J. J.; Gui, L. L.; Liu, Q. An evaluation method for the integrity of mudstone caprock in deep anticlinal traps and its application: A case study of the Sinian gas reservoirs in the central Sichuan Basin. *Acta Petrolei Sinica* **2021**, *42*, 415−427.

(12) Zhan, M. W. Quantitative Evaluation for Sealing of Caprock and the Controlling Effect in the Central Sichuan Basin. Northeast Petroleum University, Daqing, China, 2015.

(13) Wang, Y. P. Quantitative Evaluation of Effectiveness of Mudstone Caprock Sealing Natural Gas in Anyue Gas Field, Sichuan Basin. Northeast Petroleum University, Daqing, China, 2019.

(14) Li, W.; Yu, Z. J.; Wang, X. K.; Yu, Z. C.; Lu, X. S.; Feng, Q. F. Formation mechanisms of deep and ultra-deep overpressure cap rocks and their relationships with super large gas fields in the petroliferous basins of China. *Natural Gas Industry B* **2020**, *7*, 443−452.

(15) Zhang, S. Q. Evaluation on the Dynamic Evolution of Ultra-Deep Caprock in Sichuan Basin. China University of Petroleum, Beijing, 2021.
(16) Xie, Z. Y.; Wei, G. Q.; Li, J.; Xu, L.; Zhang, L.; Li, J.; Li, Z. S.; Wu, S. J.; Guo, Z. Q.; Hao, A. S. Geochemical characteristics and accumulation pattern of gas reservoirs of the Sinian-Permian in central Sichuan uplift zone, Sichuan Basin. *China Petroleum Exploration* **2021**, *26*, 50−67.
(17) Zou, C. N.; Wei, G. Q.; Xu, C. C.; Du, J. H.; Xie, Z. Y.; Wang, Z. C.; Hou, L. H.; Yang, C. L.; Li, J.; Yang, W. Geochemistry of the Sinian-Cambrian gas system in the Sichuan Basin, China. *Org. Geochem.* **2014**, *74*, 13−21.
(18) Xu, C. C.; Shen, P.; Yang, Y. M.; Luo, B.; Huang, J. Z.; Jiang, X. F.; Xie, J. R.; Cen, Y. J. Accumulation conditions and enrichment patterns of natural gas in the Lower Cambrian Longwangmiao Fm reservoirs of the Leshan-Longnüsi Paleohigh, Sichuan Basin. *Natural Gas Industry B* **2014**, *1*, 51−57.
(19) Wei, G. Q.; Du, J. H.; Xu, C. C.; Zou, C. N.; Yang, W.; Shen, P.; Xie, Z. Y.; Zhang, J. Characteristics and accumulation modes of large gas reservoirs in Sinian-Cambrian of Gaoshiti-Moxi region, Sichuan Basin. *Acta Petrolei Sinica* **2015**, *36*, 1−12.
(20) Wei, G. Q.; Xie, Z. Y.; Song, J. R.; Yang, W.; Wang, Z. H.; Li, J.; Wang, D. L.; Li, Z. S.; Xie, W. R. Features and origin of natural gas in the Sinian-Cambrian of central Sichuan paleo-uplift, Sichuan Basin, SW China. *Petroleum Explor. Dev.* **2015**, *42*, 768−777.
(21) Yang, Y. M.; Yang, Y.; Yang, G.; Song, J. R.; Wen, L.; Deng, C. G.; Xia, M. L.; Ran, Q.; Duan, G. B.; Luo, B.; et al. Gas accumulation conditions and key exploration & development technologies of Sinian and Cambrian gas reservoirs in Anyue gas field. *Acta Petrolei Sinica* **2019**, *40*, 493−508.
(22) Ma, X. H.; Yang, Y.; Wen, L.; Luo, B. Distribution and exploration direction of medium- and large-sized marine carbonate gas fields in Sichuan Basin, SW China. *Petroleum Explor. Dev.* **2019**, *46*, 1−15.
(23) Zheng, P.; Shi, Y. H.; Zou, C. Y.; Kong, L. M.; Wang, L. S.; Liu, J. Z. Natural gas sources in the Dengying and Longwangmiao Fms in the Gaoshiti-Maoxi area, Sichuan Basin. *Natural Gas Industry* **2014**, *34*, 50−54.
(24) Shuai, Y. H.; Liu, K. Y.; Hu, G. Y.; Wang, T. S.; Tian, X. W.; Zhang, B.; Chen, Z. X. Gas accumulation mechanisms of the Sinian reservoir in the Sichuan basin and their significance for deep gas exploration. *Acta Geologica Sinica* **2021**, *95*, 3400−3412.
(25) Zhou, G. X.; Qin, S. F.; Hou, Y. H.; Lu, F. The evidence of water soluble gas contribution to gas reservoir of Longwangmiao Formation in Anyue Gasfield, Sichuan Basin. *Natural Gas Geoscience* **2016**, *27*, 2193−2199.
(26) Liu, Q. Y.; Jin, Z. J.; Liu, W. H.; Gao, B.; Zhang, D. W.; Wu, X. Q.; Li, J. TSR impact on abnormal carbon and hydrogen stable isotopes in sour natural gas from marine carbonate gas fields in the eastern Sichuan Basin. *Bulletin of Mineralogy, Petrology and Geochemistry* **2015**, *34*, 471−480.
(27) He, K.; Zhang, S.; Mi, J.; Fang, Y.; Zhang, W. Carbon and hydrogen isotope fractionation for methane from non-isothermal pyrolysis of oil in anhydrous and hydrothermal conditions. *Energy Explor. Exploit.* **2019**, *37*, 1558−1576.
(28) Yang, W.; Wei, G. Q.; Wu, S. J.; Xie, W. R.; Jin, H.; Zeng, F. Y.; Hao, C. G.; Bai, Z. Z.; Su, Y. Q.; Li, R. Regional unconformities and their controls on hydrocarbon accumulation in Sichuan Basin, SW China. *Petroleum Explor. Dev.* **2023**, *50*, 573−587.
(29) Wei, G. Q. D. *Geology and Exploration of Onshore Gas in China*; Science Press, 2014.
(30) Zhao, W. Z.; Xie, Z. Y.; Wang, X. M.; Shen, A. J.; Wei, G. Q.; Wang, Z. C.; Wang, K. Sinian gas sources and effectiveness of primary gas-bearing system in Sichuan Basin, SW China. *Petroleum Explor. Dev.* **2021**, *48*, 1260−1270.
(31) *SY/T 5748−2020: Determination Method of Gas Breakthrough Pressure in Rock*; China National Petroleum Company, 2020
(32) Xie, Z. Y.; Li, Z. S.; Wei, G. Q.; Li, J.; Wang, D. L.; Wang, Z. H.; Dong, C. Y. Experimental research on the potential of sapropelic kerogen cracking gas and discrimination of oil cracking gas. *J. Nat. Gas Geosci.* **2016**, *1*, 471−479.
(33) Wang, X.; Tian, H.; Xiao, X.; Liu, D.; Min, Y.; Li, T.; Ji, S.; Peng, P. Methane-dominated gaseous inclusions in the Sinian carbonate reservoirs in central Sichuan Basin and their implications for natural gas accumulation. *Mar. Pet. Geol.* **2021**, *125*, 104871.
(34) Gao, P.; Liu, G.; Lash, G. G.; Li, B.; Yan, D.; Chen, C. Occurrences and origin of reservoir solid bitumen in Sinian Dengying Formation dolomites of the Sichuan Basin, SW China. *Int. J. Coal Geol.* **2018**, *200*, 135−152.
(35) Sweeney, J. J.; Burnham, A. K. Evaluation of a simple model of vitrinite reflectance based on chemical kinetics. *Aapg Bull.* **1990**, *74*, 1559−1570.
(36) Zou, C. N.; Du, J. H.; Xu, C. C.; Wang, Z. C.; Zhang, B. M.; Wei, G. Q.; Wang, T. S.; Yao, G. S.; Deng, S. H.; Liu, J. J.; et al. Formation, distribution, resource potential and discovery of the Sinian-Cambrian giant gas field, Sichuan Basin, SW China. *Petroleum Explor. Dev.* **2014**, *41*, 306−325.
(37) Yang, Y.; Wen, L.; Xie, J. R.; Luo, B.; Huang, P. H.; Ran, Q.; Zhou, G.; Zhang, X. H.; Wang, H.; Tian, X. W.; et al. Progress and direction of marine carbonate gas exploration in Sichuan Basin. *China Petroleum Exploration* **2020**, *25*, 44−55.
(38) Zou, C. N.; Xie, Z. Y.; Li, J.; Zhang, L.; Yang, C. L.; Cui, H. Y.; Wang, X. B.; Guo, Z. Q.; Pan, S. Q. Differences and main controlling factors of large-scale gas accumulations in typical giant carbonate gas fields: A case study on Anyue gas field in the Sichuan Basin and Jingbian gas field in the Ordos Basin. *Oil &Gas Geology* **2023**, *44*, 1−15.
(39) Li, Y. C.; Sun, Y. M.; Lan, L. Discussion on the recognition of gasorigin by using ethane carbon isotope. *Natural Gas Geoscience* **2016**, *27*, 654−664.
(40) Wang, T. S.; Geng, A. S.; Xiong, Y. Q.; Liao, Z. W.; Li, X. Kinetic simulation study on generation of gaseous hydrocarbons from the pyrolysis of marine crude oil and its asphaltene in Tarim Basin. *Acta Petrolei Sinica* **2008**, *29*, 167−172.
(41) Schoell, M. The hydrogen and carbon isotopic composition of methane from natural gases of various origins. *Geochim. Cosmochim. Acta* **1980**, *44*, 649−661.
(42) Xie, Z.; Li, J.; Li, Z.; Guo, J.; Li, J.; Zhang, L.; Dong, C. Geochemical Characteristics of the Upper Triassic Xujiahe Formation in Sichuan Basin, China and its Significance for Hydrocarbon Accumulation. *Acta Geologica Sinica (English Edition)* **2017**, *91*, 1836−1854.
(43) Ni, Y.; Liao, F.; Gao, J.; Chen, J.; Yao, L.; Zhang, D. Hydrogen isotopes of hydrocarbon gases from different organic facies of the Zhongba gas field, Sichuan Basin, China. *J. Pet. Sci. Eng.* **2019**, *179*, 776−786.
(44) Huang, S.; Duan, S.; Wang, Z.; Jiang, Q.; Jiang, H.; Su, W.; Qingfu, F.; Huang, T.; Yuan, M.; Ren, M.; et al. Affecting factors and application of the stable hydrogen isotopes of alkane gases. *Petroleum Explor. Dev.* **2019**, *46*, 518−530.
(45) Shi, Z. S.; Xie, W. R.; Ma, S. Y.; Li, G. X. Transgression sedimentary records of the members 4−6 of upper Triassic Xujiahe Formation in Sichuan Basin. *Journal of Palaeogeography* **2012**, *14*, 583−595.
(46) Orr, W. L. Changes in sulfur content and isotopic ratios of sulfur during petroleum maturation—study of big Horn Basin Paleozoic Oils. *Aapg Bull.* **1974**, *58*, 2295−2318.
(47) Zhu, L. Q.; Liu, G. D.; Song, Z. Z.; Zhao, W. Z.; Tian, X. W.; Dai, X.; Wang, Y. L.; Yang, D. L.; Li, Q.; Jiang, L.; et al. The differences in natural gas from the Dengying Formation in different areas of the north slope of the central Sichuan Paleo-uplift and its controlling factors-Taking Pengtan-1 and Zhongjiang-2 wells as examples. *Petroleum Science Bulletin* **2021**, *6*, 344−355.
(48) Stasiuk, L. D. The origin of pyrobitumens in upper Devonian Leduc formation gas reservoirs, Alberta, Canada: an optical and EDS study of oil to gas transformation. *Mar. Pet. Geol.* **1997**, *14*, 915−929.
(49) Zhang, S. C.; He, K.; Wang, X. M.; Hu, G. Y.; Zhang, B.; Mi, J. K.; Su, J. The multi-path gas generation model and its potential

contribution to petroleum accumulation in deep formations. *Natural Gas Geoscience* **2021**, *32*, 1421−1435.

(50) Yuan, Y. S.; Hao, Y. Q.; Liu, Q. Y.; Gao, J.; Zhang, S. Q. TSR hydrocarbon loss assessment: I. main controlling factors and intensity indicators of TSR. *Marine Origin Petroleum Geology* **2021**, *26*, 97−104.

(51) Wilson, N. S. F. Organic petrology, chemical composition, and reflectance of pyrobitumen from the El Soldado Cu deposit, Chile. *Int. J. Coal Geol.* **2000**, *43*, 53−82.

(52) Rimmer, S. M.; Crelling, J. C.; Yoksoulian, L. E. An occurrence of coked bitumen, Raton Formation, Purgatoire River Valley, Colorado, USA. *Int. J. Coal Geol.* **2015**, *141−142*, 63−73.

(53) Tian, H.; Xiao, X.; Wilkins, R. W. T.; Tang, Y. New insights into the volume and pressure changes during the thermal cracking of oil to gas in reservoirs: Implications for the in-situ accumulation of gas cracked from oils. *Bulletin* **2008**, *92*, 181−200.

(54) Tian, H.; Lu, X. S.; Zhang, S. C.; Liu, S. B.; Tian, X. W.; Ma, X. Z.; Liu, Q. Multilayer caprock natural gas diffusion capacity of Longwangmiao Formation gas reservoir in Anyue gas field, Sichuan Basin. *Acta Petrolei Sinica* **2022**, *43*, 355−363 398.

(55) Ali, M.; Ma, H. L.; Pan, H. P.; Ashraf, U.; Jiang, R. Building a rock physics model for the formation evaluation of the Lower Goru sand reservoir of the Southern Indus Basin in Pakistan. *J. Pet. Sci. Eng.* **2020**, *194*, 107461.

(56) Ashraf, U.; Anees, A.; Shi, W.; Wang, R.; Ali, M.; Jiang, R.; Vo Thanh, H.; Iqbal, I.; Zhang, X.; Zhang, H. Estimation of porosity and facies distribution through seismic inversion in an unconventional tight sandstone reservoir of Hangjinqi area, Ordos basin. *Front. Earth Sci.* **2022**, *10*, 1014052.

https://doi.org/10.1021/acsomega.3c10109
ACS Omega 2024, 9, 23390−23399