Geochemical characteristics and accumulation model of Devonian natural gas in Northwestern Sichuan Basin, China

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Abstract: Gas exploration has made major breakthrough firstly in Devonian strata in northwest Sichuan Basin, and its natural gas source have attracted much attention. In this work we developed comprehensive researches on natural gas geochemistry, reservoir bitumen and related source rock biomarkers of Devonian. Result shows: Natural gas in Devonian is secondary cracking gas dominated by hydrocarbon gas. It is major in sapropelitic type gas and comes from the source rock of Qiongzhusi Formation of Lower Cambrian and Middle Permian, mainly from the former. There are two reservoir accumulation model for gas in Devonian: lower source to upper reservoir and upper source to lower reservoir. Result is of important guidance significance for the exploration deployment of natural gas in this area.

1. Introduction
Sichuan Basin is a large and superimposed petroliferous basin with multilayered reservoirs. It has more than 20 gas-productive reservoirs from Sinian to Jurassic [1-2]. Devonian strata are only distributed in the west of the Basin, and lots of oil sands and bitumen have been found in field outcrop section in Devonian during the early stage. Some scholars have researched the source of these oil sands and bitumen, and there are many viewpoints. Some believe that they are mainly from the source rock of Lower Cambrian [3], while others believe they are from black shale of Lower Cambrian and Lower Silurian [4]. In 2016, ST3 Well in Shuangyushi Structure firstly obtained industrial gas flow with daily production of 11.6×10$^4$ m$^3$ in 7569~7601.5m well section for dolomite reservoir in Guanwushan Formation of Middle Devonian Series (D$_2g$), which opened the prologue of natural gas exploration in Devonian within the basin [5]. Afterwards, natural gas flow with daily production of about (1-4)×10$^4$ m$^3$ was obtained in Zongchanggou Formation in Carboniferous System - Guanwushan Formation in Middle Devonian (7716~7761m of ST7 Well) and Guanwushan Formation(7555~7591m of ST10 Wel). Moreover, residual bitumen after lots of crude oil cracked into gas could be seen during drilling all wells meet Guanwushan Formation, which showed the excellent natural gas exploration prospects of super-deep field in Devonian of the area. However, sources of these natural gas and bitumen were not clear.
2. Geological background of gas accumulation model

Research area is located in the northwest of Sichuan Basin (Figure 1). Sichuan Basin is a large superimposed basin developing from the upper Yangtze Craton, experiencing stages for marine facies in late Proterozoic - middle Triassic Epoch - late Triassic epoch - Cenozoic terrestrial deposit basin[1]. Its tectonic movements mainly include Chengjiang, Tongwan, Caledonian, Liukiang, Yunnan, Tungwu, Indosinian, Yanshan and Himalayan movements [2]. These tectonic movements have a profound influence on basin deposition, diagenesis and oil-gas accumulation, resulting in Sichuan Basin characterized by multiple development of bed series, accumulation combinations and production layers of source rock etc.

Marine bed series in northwest Sichuan develops multiple sets of high-mature over-mature source rock with different organic matter types, mainly including: ① shale in Qiongzhusi Formation of Lower Cambrian distributed in the region[6], with general thickness of 50~300m and mid-depth of 250~300m[7]; content of Kerogen carbon isotope (δ¹³C_K) is -33.5‰~ -32.3‰, and average content is -32.8‰; equivalent vitrinite reflectance (Ro) is 3.0%~4.0%. ② Thicknesses of muddy limestone in Qixia Formation and Maokou Formation of Middle Permian distributed in the region are respectively 10~30m and 40~140m; δ¹³C_K are respectively 30.7‰~28.3‰ (average value is 29.5‰) and -32.8‰~28.5‰ (average value is -30.9‰); Ro’ is 2.0%~2.5%. ③ In terms of shale and coal in Liangshan Formation of Lower Permian distributed in the region with thin depth, shale thickness is 1-3m, and thickness of coal bed is 0.5-1.5m; shale δ¹³C_k is -26.7‰~23.6‰, and the average value is -25.3‰. Evolution degree is basically equal to that in Qixia Formation [8]. ④ Shale in Longmaxi Formation of Lower Silurian Series locally distributed is absent in general area of west Sichuan, and thickness in the east of research area is generally 30-50m. δ¹³C_K is -30.7‰~29.9‰, and the average value is -30.2‰. Ro’ is 2.6%~3.5%.

![Figure 1. Pre-sedimentary paleogeological map of Devonian (revised according to document 5).](image)

3. Test and discussion

3.1 Composition of natural gas

In terms of natural gas in Guanwushan Formation of Middle Devonian in northwest Sichuan, samples in ST3 Well and ST7 Well can be collected at present, and composition analysis data of natural gas is shown in Table 1. Natural gas in Guanwushan Formation is dry gas dominated by hydrocarbon gas. Hydrocarbon gas contains 91.96%-96.96% methane, and a small amount of ethane (0.13%-0.23%) and trace amount of propane (0.008%-0.011%). Drying coefficient of natural gas (C₁/C₁⁺) is 0.9975-0.9985, belonging to typical dry gas. Non-hydrocarbon gas includes carbon dioxide, nitrogen, helium, hydrogen and hydrogen sulfide etc., 2.12%~6.36%, 0.61%~2.38%, 0.02%~0.04%, 0.01%~0.27% and 0.01%~0.27% respectively.
From the path of natural gas formation, natural gas in Guanwushan Formation belongs to secondary cracking gas of liquid hydrocarbon which has generated by source rock. Bitumen with higher abundance (content is 0.5%~2.7%) and higher evolution degree (average value of bitumen reflectance is 2.64%~2.94%) in reservoir of Guanwushan Formation is one of the important basis of secondary cracking gas, and has the similar characteristics with typical secondary cracking gas[9-10] in Dengying Formation- Longwangmiao Formation in palaeo higher Gaoshiti-Moxi Region (hereafter referred to as Gaomo Region, the same below), that is ln(C\textsubscript{in} Dengying Formation- Longwangmiao Formation in palaeo higher Gaoshiti-Moxi Region) secondary cracking gas, and has the similar characteristics with typical secondary cracking gas[9-10] in Dengying Formation- Longwangmiao Formation in palaeo higher Gaoshiti-Moxi Region (hereafter referred to as Gaomo Region, the same below), that is ln(C\textsubscript{in} Dengying Formation- Longwangmiao Formation in palaeo higher Gaoshiti-Moxi Region). The humidity value are controlled by thermal evolution degree and parent material type of syngas[15]. The humidity value becomes higher with the decline in humidity coefficient, which shows that δ\textsubscript{13}C value is obviously heavier than that of sapropel-type gas (δ\textsubscript{13}C\textsubscript{2} < -32‰) in Huanglong Formation of Carboniferous System, east Sichuan mainly from shale in Qiongzhusi Formation and marl in Middle Permian System- Cambrian system[11], with the highest thermal evolution degree; natural gas in Guanwushan Formation is not only due to cracking for liquid hydrocarbon generated by source rock in Qiongzhusi Formation of Cambrian System, but also due to cracking of liquid hydrocarbon generated by source crack in Middle Permian Series, which is a kind of mixed source cracking. Thermal evolution degree is undoubtedly lower than Gaomo natural gas, but higher than that of natural gas in Huanglong Formation of Carboniferous System in east Sichuan from Longmaxi Formation of Lower Silurian Series [12].

### 3.2 Composition of gas carbon isotope

Analysis result of gas carbon isotope in Guanwushan Formation of Devonian in northwest Sichuan is shown in Table 1. Value of methane carbon isotope of natural gas (δ\textsuperscript{13}C\textsubscript{1}) is -32.3‰~30.7‰, and value of ethane carbon isotope (δ\textsuperscript{13}C\textsubscript{2}) is -28.4‰~28.6‰, with differences between two kinds of typical natural gases. Namely, δ\textsuperscript{13}C\textsubscript{2} value is obviously heavier than that of sapropel-type gas (δ\textsuperscript{13}C\textsubscript{2} < -32‰) in Huanglong Formation of Carboniferous System, east Sichuan mainly from shale in Longmaxi Formation of Silurian System[12] and in Gaomo Longwangmiao Formation mainly from shale in Qiongzhusi Formation of Cambrian System[11], and lighter than that of humus-type natural gas (δ\textsuperscript{13}C\textsubscript{2} > -25‰) in Yuanba[13], Longgang[14] Changxing Formation-Feixianguan Formation mainly from source rock of Upper Permian Series, similar to partial sapropel-humic type natural gas (Figure 2b); δ\textsuperscript{13}C\textsubscript{1} value is also between two kinds of natural gas, characterized by mixed gas. From the relevance between values of natural gas δ\textsuperscript{13}C\textsubscript{1} and δ\textsuperscript{13}C\textsubscript{2} and humidity coefficient, there is tendency that value becomes higher with the decline in humidity coefficient, which shows that δ\textsuperscript{13}C\textsubscript{1} and δ\textsuperscript{13}C\textsubscript{2} value are controlled by thermal evolution degree and parent material type of syngas[15]. The humidity coefficient (C\textsubscript{2}/C\textsubscript{1}) of natural gas in Guanwushan Formation is roughly equivalent to Longwangmiao Formation, but δ\textsuperscript{13}C\textsubscript{1} and δ\textsuperscript{13}C\textsubscript{2} value are higher than the latter. Under the condition that evolution degree is roughly equivalent, this mainly reveals the difference in parental materials of syngas between both. From the analysis on accumulation geological conditions, there are fractures communicating reservoir in Guanwushan Formation and source rock in Qiongzhusi Formation, and gas oil generated in Middle Permian Series can enter reservoir in Guanwushan Formation through source-reservoir docking side of two walls of fault. Therefore, source rock making greater contribution to gas reservoir in Guanwushan Formation is mainly from shale in Qiongzhusi Formation and marl in Middle Permian Series.

### Table 1. Gas Composition and Carbon and Hydrogen Isotope in Devonian of Northwest Sichuan.

| Well | Depth (m) | CH\textsubscript{4} | C\textsubscript{2}H\textsubscript{6} | C\textsubscript{3}H\textsubscript{8} | CO\textsubscript{2} | N\textsubscript{2} | He | H\textsubscript{2}S | CH\textsubscript{4} | C\textsubscript{2}H\textsubscript{4} | CH\textsubscript{2} | δ\textsuperscript{13}C (%) | δ\textsuperscript{13}H (%) | Data source |
|------|-----------|----------------|----------------|----------------|-------------|--------|----|--------|--------|----------------|-------------|-------------|-------------|-----------|
| ST3  | 7569-7601 | 96.96 0.23 0.010 2.12 0.61 0.02 0.05 0.01 -32.3 -28.4 -139 | | | | | | | | | | | | | 8 Refs |
| ST3  | 7716-7761 | 94.12 0.21 0.011 2.31 1.70 0.02 0.01 0.01 -31.9 -28.4 -141 | | | | | | | | | | | | | |
| ST7  | 91.96 0.13 0.008 6.36 0.98 0.04 0.27 0.27 -30.7 -28.6 -136 | | | | | | | | | | | | | this text |
Series, and supply of gas with multiple source and multiple types causes mixed type of natural gas for gas-reservoir at present.

![Figure 2](image-url)  
**Figure 2.** Geochemical Characteristics of Natural Gas in Devonian of Northwest Sichuan Basin. Remarks: (a) Recognition of Kerogen Degradation Gas and Crude Oil Cracking Gas (modified in accordance with Literature 8); (b) Relationship of Natural Gas $\delta^{2}H_1 - (C_{2}^{+}/C_{1.3})$; (c) Relationship of Natural Gas $\delta^{2}H_1 - \text{H}_2\text{S}$.

### 3.3 Composition of gas hydrogen isotope

Analysis result of gas hydrogen isotope in Guanwushan Formation is shown in Table 1. Value of methane hydrogen isotope of natural gas ($\delta^{2}H_1$) is -141‰~ -136‰, and ethane hydrogen isotope ($\delta^{2}H_2$) is not detected. Subtle changes in $\delta^{2}H_1$ value may be related to difference in its humidity coefficient and hydrogen sulfide content. For natural gas samples in the same series, $\delta^{2}H_1$ value has the tendency that it becomes lighter with the increase in humidity coefficient (Figure 2c) and heavier with the increase in hydrogen sulfide content (Figure 2d).

### 3.4 Characteristics of bitumen n-alkanes

Saturated hydrocarbon n-alkanes of bitumen in Guanwushan Formation of Devonian in ST3 Well presents the distribution characteristics of double main peaks, and carbon number is between nC$_{13}$~ nC$_{31}$ (Figure 3a). Main peaks are nC$_{17}$ and nC$_{25}$ respectively, and nC$_{17}$~nC$_{25}$, nC$_{22}$/nC$_{22}^+$ ratio is 1.26, and Pr/Ph ratio is 0.56. Ratios of Pr/nC$_{17}$ and Ph/nC$_{18}$ are 0.62 and 1.25 respectively.

![Figure 3](image-url)  
**Figure 3.** Characteristics of Bitumen Biomarkers in Devonian of ST3 Well of Northwest Sichuan Basin. (a) n-alkanes characteristics; (b) terpane characteristics; (c) sterane characteristics.

Although bitumen in Guanwushan Formation is in the stage of over-mature evolution, and bitumen
reflectivity is 2.94%, contribution of parental materials of carbon number biogenesis in two categories can be seen from the double main-peak distribution characteristics of its n-alkanes.

3.5 Characteristics of terpane and sterane
Reservoir bitumen in Guanwushan Formation of Devonian of ST3 Well is rich in tricyclic terpane and pentacyclic triterpene compounds (Figure 3b), and ratio of tricyclic terpane/ pentacyclic triterpene is 0.30. Biological precursor of tricyclic terpane is prokaryote (bacteria and blue-green algae), and it has higher thermal stability and resistance to biodegradation than hopane [16]. The sample is not biodegraded, and abundant tricyclic terpane is mainly related to maturity.

C_{21} pregnane abundance of reservoir bitumen is higher than C_{22} pregnant sterane, and ratio of C_{21}/C_{22} is 1.78, mainly related to high maturity of organic matters. C_{27}, C_{28} and C_{29} regular sterane present phenomenon of C_{29}≈C_{27}>C_{28} (Figure 3c). Sterane distribution characteristics of bitumen in Guanwushan Formation is between marl in Maokou Formation and Qixia Formation and shale in Qiongzhusi Formation and Longmaxi Formation, presenting characteristics of mixed source.

4. Reservoir-forming model of oil gas
According to geological background and conditions of reservoir forming in Devonian in northwest Sichuan, gas in Devonian have two kinds of movement and gathering modes (Figure 4): on one hand, oil gas generated by deep source rock in Lower Cambrian Series is made to move upwards through large deep fault, and gathered in the favorable reservoir parts to form the model of old source in young reservoir. On the other hand, strong tectonic movement makes middle structural layer in northwest Sichuan extrude and fold, concomitant with fault block. Docking for source-reservoir rock layer in two walls of fault makes oil gas generated by source rock of Middle Permian Series enter reservoir in Devonian through fault side to form the model of young source in old reservoir. Strong extruding and lifting generated by tectonic movement during Yanshan Period-Himalayan Period do not affect old gas reservoir gathered in No. ① fault footwall, because past-salt rock in overlaying super-thick low-middle Triassic Series can effectively cover.

![Figure 4](image)

**Figure 4.** Accumulation Model of Natural Gas in Devonian in Northwest Sichuan, China.

5. Conclusion
Natural gas of Devonian in northwest Sichuan is secondary cracking dry gas dominated by methane, containing a small amount of carbon dioxide, nitrogen and other non-hydrocarbon gas, and a small amount of hydrogen sulfide. It is mainly mixed gas. Natural gas and bitumen in Devonian display characteristics of mixed source and has characteristics of source-mixed gas reservoir forming of multisource hydrocarbon. There are mainly two kinds of accumulation models. Firstly, it is to communicate underlie source rock in Qiongzhusi Formation through deep fault; secondly, oil gas generated by source rock in Middle Permian Series enters reservoir in Devonian through lateral docking of source rock-reservoir at two sides of fault.

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