Research Article

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Insights into origins of the natural gas in the Lower Paleozoic of Ordos basin, China

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Abstract: Based on natural gas compositions, carbon isotope ratios, and geological analysis, the genesis and origin of gases in the Lower Paleozoic of Ordos basin are discussed. Due to differences in distribution and genesis, the gases in Lower Paleozoic were divided into five types, namely western margin gas, weathered crust gas, pre-salt gas, Ordovician deep gas, and Cambrian gas. The results show that the $\delta^{13}\text{C}_1$ and $\delta^{13}\text{C}_2$ of western margin gas range from -35.6 to -38.9‰ and from -27.2 to -35.9‰ , respectively, indicating oil-type gas and mainly from the O_1k and O_2w marine source rocks. The $\delta^{13}\text{C}_1$ of weathered crust gas varies from -31.2 to -37.8‰ , but $\delta^{13}\text{C}_2$ is mostly around -25.0‰ , which indicates weathered crust gas originates from the Carboniferous–Permian coal-measure source rocks. In contrast, $\delta^{13}\text{C}_1$ and $\delta^{13}\text{C}_2$ in the pre-salt strata are mostly less than -30.0‰ . Yet its distribution of $\Delta(\delta^{13}\text{C}_2 - \delta^{13}\text{C}_1)$ is from -1.7 to 13.6‰ , and $\text{C}_1/\text{C}_2 + \text{C}_3$ is of $6.68\text{--}4372.50$. These indicate that the pre-salt gas is mainly high-over mature oil cracking gas from the O_1m marine source rock. The $\delta^{13}\text{C}_1$ of Ordovician deep gas is

averaging -39.4‰ , and $\delta^{13}\text{C}_2$ varies from -25.4 to -33.0‰ , which imply coexistence of oil-type and coal-type gas. It is presumed that the C–P coal-type gas may migrate into and accumulate at Ordovician deep reservoirs through unconformity and fault. The $\delta^{13}\text{C}_2$ and $\Delta(\delta^{13}\text{C}_2 - \delta^{13}\text{C}_1)$ of Cambrian gas are both the most negative, respectively, averaging -34.9‰ and averaging -3.2‰ , indicating over-mature oil-type gas. Formation and evolution of the Qingyang paleo-uplift result in that the Cambrian gas mainly comes from the Cambrian or Ordovician marine source rocks in the southern basin.

Keywords: natural gas origin, natural gas source, hydrocarbon accumulation mode, Lower Paleozoic, Ordos basin

1 Introduction

Origins and sources of natural gas have always been the focus of attention for geochemists. Origins of natural gas are generally analyzed by the composition content, dryness coefficient ($\text{C}_1/\Sigma\text{C}_{1-5}$), and carbon isotope of methane ($\delta^{13}\text{C}_1$), ethane ($\delta^{13}\text{C}_2$), and propane ($\delta^{13}\text{C}_3$), etc., in the natural gas [1–3]. However, with the increase of natural gas maturity, and the sedimentary environment in which the gas source rock is formed becomes more complex, the origins and sources of the natural gas have eventually become a puzzle that is hard to solve. Considering the Ordovician natural gas in the Jingbian gas field of the Ordos basin as an example, some scholars believed that the weathering crust reservoir at the top of the Majiagou formation directly contacts with the Upper Paleozoic Carboniferous–Permian (C–P) coal-measure source rock, from which the natural gas is considered as the coal-type gas, and from C–P source rock [1,4,5]; some other scholars regarded that the natural gas is of mixed origins, with contributions from both the C–P coal-measure source rock and marine Ordovician Majiagou source rock [6]; and some other scholars even believed that it should be oil-type gas mainly from the Majiagou source rock [7]. The focus of the debate is that the distribution ranges of $\delta^{13}\text{C}_1$ and $\delta^{13}\text{C}_2$ in the Ordovician natural gas in the Jingbian gas

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field are relatively large, spanning the distribution ranges of both the coal-type gas and oil-type gas, which makes it more difficult to distinguish genesis of the natural gas. To solve this problem, multiple methods have been adapted and some research progresses have been made. For instances, Liu et al. [8] discussed the origins of the natural gas with respect to distribution and thermal evolution of source rocks, and Cai et al. [6] analyzed the sources of the natural gas from the perspective of thermo-chemical sulfur reduction.

The pre-salt reservoir under the Ordovician weathering crust has a long vertical distance from the C–P coal-measure source rock; moreover, an interval of gypsum salt rock with certain thickness exists between the pre-salt reservoir and the coal-measure source rock. Hence, the Upper Paleozoic C–P coal-type gas is difficult to flow downward into the pre-salt reservoir. However, $\delta^{13}\text{C}_1$ of some pre-salt gas shows the characteristics of coal-type gas [9]. Therefore, clarifying the origins and sources of the natural gas directly affects the exploration direction of the Lower Paleozoic or deep strata in the Ordos basin. In view of this, based on the C–P coal-type gas and the natural gas in various Lower Paleozoic strata, this study compared and analyzed the components and carbon isotopes of different natural gases in the Lower Paleozoic and the C–P coal-type gas, discussed the origins of the natural gas, and clarified the sources of the natural gas in combination with geological analysis to provide a scientific basis for the deployment of the natural gas exploration in the Lower Paleozoic or deep strata of the Ordos basin.

2 Geologic background

The Ordos basin, located in central China, is the second largest sedimentary basin of China [8]. It has plentiful natural gas resources in the Paleozoic strata. After years of exploration, two giant gas field (Sulige and Jingbian) with trillions of natural gas resources have been found. The Jingbian giant gas field is located in the middle of the Ordos basin and is typically weathering crust gas reservoir at the top of the Majiagou formation (O_1m); the Sulige giant gas field, located in the northwest of the Jingbian giant gas field, features the Upper Paleozoic C–P gas reservoir, a typical coal-type gas reservoir (called C–P gas) [8] (Figure 1). Usually, giant gas field is often closely related to the distribution of high-quality source rocks. Influenced by the lithofacies and paleogeographic during the Paleozoic Era, the distribution of the Lower Paleozoic source rock in the Ordos basin has some unique features. During the Cambrian, the Ordos basin was uplifted as a whole, and only a Northeast-trending gulf developed in the southern basin, which controls the distribution of

marine source rocks of the Dongpo formation (C_1d) and the Luoquan formation (C_1l) at the base of the Cambrian system [10]. The lower Cambrian marine source rock has high organic matter with a broad range from 0.12 to 9.39% (average: 2.68%), and the T_{max} of the source rocks is up to 544°C, which indicate that the source rocks have relatively high thermal maturity [10]. During the Ordovician period, the eastern part was mainly controlled by the North China Sea, accepting primarily carbonate-platform sediments; the western part was controlled by the Qilian Sea, with deposition of the deeper-water trough environment; the Qilian Sea was separated from the North China Sea by the central paleo-uplift [11]. Therefore, the source rocks of the Ordovician Pingliang formation (O_2p) are mainly distributed in the western and southern margins of the basin. The cumulative thickness of argillaceous source rock is 100–200 m, and the total organic carbon (TOC) is from 0.01 to 3.30% [12]. The TOC of O_1k and O_2w marine source rocks range from 0.03 to 4.55% [12]. While the source rocks of the Majiagou Formation (O_1m) are distributed in the mid-eastern basin. The cumulative thickness of source rock is greater than 40 m, and the TOC ranges from 0.18 to 7.48% [12]. During the C–P periods, the basin experienced transition from the marine to continental environments, and developed coal-measure source rocks in the whole basin. The C–P coal-measure source rock has stable distribution and high organic abundance (total organic carbon of coal seams is of 70.8–83.2%, whereas that of dark mudstone is of 2–3%), and the R_o of the source rock all exceeds 1.5%. The C–P coal-measure source rock is characterized by its extensive hydrocarbon generation and large-area gas supply [11].

In addition, during the late Caledonian orogeny, the Ordos basin was uplifted as a whole and suffered 150 Ma of weathering and erosion, which resulted in the absence of the Silurian–Early Carboniferous–Late Ordovician deposits and formed a regional unconformity at the top of the Ordovician system [11]. This makes the Upper Paleozoic C–P coal-measure source rock directly contact with the Lower Paleozoic Ordovician and even the Cambrian strata in some areas. Therefore, the Lower Paleozoic carbonate rocks have sufficient gas sources. The distribution of natural gas in the Lower Paleozoic has obvious differences in different areas of the Ordos basin, due to varied source-reservoir rock configurations. At present, the natural gas discovered in the Lower Paleozoic is mainly distributed in the Lower Ordovician Kelimoli formation (O_1k) and the Middle Ordovician Wulalike formation (O_2w) in the west margin (called western margin gas), the Lower Ordovician Ma_5^{1-4} submembers ($\text{O}_1\text{m}_5^{1-4}$) in the mid-eastern part (named weathered crust gas), the pre-salt strata ($\text{O}_1\text{m}_5^{6-10}$) in the Lower Ordovician Majiagou formation (called pre-salt gas)

Figure 1: Distribution of pre-Carboniferous geologic structural units and vertical distribution of natural gas in the Lower Paleozoic of Ordos basin (modified from ref. [12]).

and the deeper Ordovician Ma_3 – Ma_4 Members (O_{m3-4}) (called Ordovician deep gas) in the mid-eastern part, and the Cambrian system in the south of the Ordos basin (named Cambrian gas; Figure 1).

3 Samples and experiments

Forty-seven gas samples were considered in this study. They were obtained from the PetroChina Changqing Oil-field Company, including 7 western margin gas samples, 13 pre-salt gas samples, 7 Ordovician deep gas samples, 16 weathered crust gas samples, and 4 Cambrian gas samples. Gas composition and carbon isotopes were measured by HP6890 GC (Spectra Lab Scientific Inc.) and Finnigan MAT Delta S mass spectrometer (Finnigan Mat

Company) in National Engineering Laboratory of Low Permeability Oil and Gas Field Exploration and Development with the conditions provided by Han et al. [13].

4 Results and discussion

4.1 Origins of natural gas

The carbon isotope of natural gas is the main parameter to classify the genetic type of natural gas. The methane and ethane carbon isotope distribution of natural gases involved in this study is shown in Table 1. The carbon isotope of natural gas is often affected by other alteration. There is a good positive correlation between the $\ln(C_1/C_2)$

Table 1: The carbon isotope values of natural gas from Lower Paleozoic in Ordos basin

No.	Types	Carbon isotope of methane (‰, VPDB)	Carbon isotope of ethane (‰, VPDB)	$\Delta^{13}\text{C}_{2-1}$ (‰, VPDB)
1	Western margin gas	−38.9 to −35.6‰/−37.1‰	−35.9 to −27.2‰/−31.9‰	0.3–11.8/5.2
2	Weathered crust gas	−37.8 to −31.2‰/−34.5‰	−39.4 to −22.6‰/−29.7‰	−5.7 to 12.9/4.7
3	Pre-salt gas	−39.5 to −32.2‰/−34.6‰	−35.0 to −22.8‰/−30.5‰	−1.7 to 13.6/4.2
4	Ordovician deep gas	−42.3 to −36.7‰/−39.4‰	−33.0 to −25.4‰/−29.1‰	4.3–16.9/10.9
5	Cambrian gas	−35.3 to −29.9‰/−32.1‰	−38.2 to −36.9‰/−37.6‰	−9.2 to 7.1/−4.4

and $\delta^{13}\text{C}_1$ – $\delta^{13}\text{C}_2$ for the natural gas in this study (Figure 2), this distribution trend is consistent with the natural gas without strong alteration determined by Prinzhofer and Huc [14], which is indicating that the isotopic characteristics of natural gas are mainly affected by maturity, and it is not obviously affected by other alteration [14].

Figure 3 is the cross plot of $\delta^{13}\text{C}_1$ and $\delta^{13}\text{C}_2$ of the Lower Paleozoic natural gas in the Ordos basin. As reflected by this figure, it is difficult to distinguish the Lower Paleozoic natural gas by $\delta^{13}\text{C}_1$ alone because the ranges of $\delta^{13}\text{C}_1$ have a large overlap in the Lower Paleozoic natural gas and C–P coal-type gas. However, the $\delta^{13}\text{C}_2$ is quite different. The C–P coal-type gas have heavier $\delta^{13}\text{C}_2$ (from −21.7 to −27.6‰, averaging −24.2‰), and oil-type gas have lighter $\delta^{13}\text{C}_2$ distribution range (from −28.5 to −39.4‰). If a slope value of one is considered as the threshold, oil-type gas can be divided into two categories, namely, the positive-sequence oil-type gas (characterized by $\delta^{13}\text{C}_1 < \delta^{13}\text{C}_2$) and reverse-sequence oil-type gas (characterized by $\delta^{13}\text{C}_1 > \delta^{13}\text{C}_2$). Generally, the positive-sequence natural gas represents a normal organic origin natural gas, whereas the reverse-sequence natural gas has numerous explanations for origins, such

as mixing of natural gas, migration fractionation of natural gas, and biodegradation [1,15–18]. Compared with other types of natural gas, the $\delta^{13}\text{C}_2$ of the Cambrian gas is generally the lightest, with a limited distribution range (mainly from −38.2 to −36.9‰; Table 1), showing the characteristics of reverse-sequence oil-type gas. The $\delta^{13}\text{C}_1$ and $\delta^{13}\text{C}_2$ distribution ranges of the western margin gas are relatively narrowed, with lighter $\delta^{13}\text{C}_1$ and $\delta^{13}\text{C}_2$ values, indicating typical positive-sequence oil-type gas. However, most of the weathered crust gas in the middle-eastern parts present the distribution ranges of $\delta^{13}\text{C}_1$ and $\delta^{13}\text{C}_2$ of similar to those of the C–P coal-type gas, whereas a few are found similar to oil-type gas. This indicates that the weathered crust gas is dominated by coal-type gas, yet with a few from oil-type gas, which is in better agreement with other researchers' understanding of the origin of the weathered crust gas [8]. The $\delta^{13}\text{C}_2$ distribution range of pre-salt gases is from −22.8 to −35.0‰, showing characteristics of both coal-type and oil-type gases. However, the $\delta^{13}\text{C}_1$ of the Ordovician deep gas is the lightest among Lower Paleozoic natural gases (from −36.7 to −42.3‰, averaging −39.4‰), whereas $\delta^{13}\text{C}_2$ ranges from −25.4 to −33.0‰, with part of samples corresponding to C–P coal-type gas and another part to oil-type gas.

Figure 2: Cross plot of $\ln(\text{C}_1/\text{C}_2)$ and $\delta^{13}\text{C}_1$ – $\delta^{13}\text{C}_2$ of natural gas in the Lower Paleozoic of Ordos basin.

Figure 3: Cross plot of $\delta^{13}\text{C}_1$ and $\delta^{13}\text{C}_2$ of natural gas in the Lower Paleozoic of Ordos basin.

The carbon isotope ratio difference between ethane and methane (hereinafter referred to as $\Delta(\delta^{13}\text{C}_2 - \delta^{13}\text{C}_1)$) in natural gas is related to maturity of natural gas, and it declines with the increasing of gas maturity [3,7]. During the highly mature evolution stage ($R_o = 1.3\text{--}2.0\%$), $\Delta(\delta^{13}\text{C}_2 - \delta^{13}\text{C}_1)$ is typically about 12‰, and it then reverses to be negative during the late period of the over-mature stage. According to the distribution range of the Lower Paleozoic natural gas, the boundary between the highly mature and

over-mature stages is set at 5‰ [19]. Obviously, it is easy to differentiate oil-type gas from coal-type gas in the cross plot of $\Delta(\delta^{13}\text{C}_2 - \delta^{13}\text{C}_1)$ versus $\delta^{13}\text{C}_1$ (Figure 4). Oil-type gas is between the two dashed lines and others are for coal-type gas. Moreover, it is easy to draw the conclusion that the thermal evolution degrees of the Lower Paleozoic natural gas are relatively high. The $\Delta(\delta^{13}\text{C}_2 - \delta^{13}\text{C}_1)$ less than 0 suggests reverse-sequence natural gas. Comparative analysis shows that reverse-sequence

Figure 4: Cross plot of $\delta^{13}\text{C}_1$ and $\Delta(\delta^{13}\text{C}_2 - \delta^{13}\text{C}_1)$ of natural gas in the Lower Paleozoic of Ordos basin.

natural gas exists only in the Cambrian gas, weathered crust gas, and pre-salt gas. The Cambrian gas and some weathered crust gas have the lowest $\Delta(\delta^{13}\text{C}_2 - \delta^{13}\text{C}_1)$ value, which indicates that the thermal evolution of natural gas has reached the over-mature stage. It is speculated that the weathered crust gas does also have the characteristics of mixed highly mature coal-type and over-mature oil-type gas. The Cambrian gases are mainly over-mature oil-type gas, whereas the pre-salt gases are mainly high-over mature oil-type gas, with a small portion classified as coal-type gas. On an overall basis, for the Lower Paleozoic natural gas of the Ordos basin, the evolution degree of natural gas increases with depth. The C-P coal-type gas and weathered crust gas have the lowest maturity, which is consistent with the understanding that the weathered crust gas mainly comes from coal-measure source rocks. Nevertheless, the Ordovician deep gas in the Ma_3 – Ma_4 members is very special, as some samples present very high $\Delta(\delta^{13}\text{C}_2 - \delta^{13}\text{C}_1)$ values, even higher than that of the C-P coal-type gas. It is presumed that part of the Ordovician deep gas comes from the coal-measure source rock. The $\Delta(\delta^{13}\text{C}_2 - \delta^{13}\text{C}_1)$ value of western margin gas is primarily presenting the feature of high-over mature oil-type gas (Figure 4).

Dai [20] divided the origins of natural gas into ten types according to $\text{C}_1/\text{C}_2 + \text{C}_3$ and $\delta^{13}\text{C}_1$ of the natural gas. Normally, the amount of natural gas generated by cracking of crude oil per unit mass is two to four times of the total amount of gas generated by Type-III kerogen per unit mass [21]. Therefore, it may be more meaningful

for natural gas exploration to search for crude oil cracking gas in deep layers of the basin. It can be seen from Figure 5 that the Lower Paleozoic natural gas mostly lies in Zones II and III. The weathered crust gas is mainly in Zone II₂ of crude oil cracking gas and Zone III₁ of mixed crude oil cracking and coal-type gases. That is, the weathered crust gas contains both crude oil cracking and coal-type gases, which may be one of the reasons for the natural gas resource of the Jingbian gas field can be high up to trillions of cubic meters. Interestingly, the distribution of the pre-salt gas is similar to that of the weathered crust gas, mainly in Zones II₂ and III₁; recently, a natural gas well with daily production over one million cubic meters from the pre-salt layer is also in Zone III₁. These imply that the resource potential of crude oil cracking gas should be not ignored. As for the Ordovician deep gas, data are limited, with one point located in the crude oil cracking gas zone and two at the boundary between the oil-type gas zone and the zone of mixed condensate oil associated gas and coal-derived gas, and these results are similar to the results reflected by Figures 3 and 4. In Figure 5, the western margin gas are mainly in Zones III₁, it seems related to oil cracked gas and coal-derived gas, which is different from the results reflected by Figures 3 and 4.

4.2 Distribution of natural gas

The $\delta^{13}\text{C}_2$ of natural gas is considered to be related to types of sedimentary organic matter, and thus is often

Figure 5: Identification of different types of natural gas in the Lower Paleozoic of the Ordos basin (modified from an earlier study [20]).

used to identify the origin of natural gas [19]. It is generally considered that ethane carbon isotope greater than -27.5‰ is coal-type gas and less than -27.5‰ is oil-type gas [22]. The cross plot of $\Delta(\delta^{13}\text{C}_2-\delta^{13}\text{C}_1)$ versus $\delta^{13}\text{C}_2$ in natural gas can be used to determine natural gas maturity and origin. Figure 6 clearly shows that the Lower Paleozoic natural gas of the Ordos basin was divided into oil-type gas (the left part) and coal-type gas (the right part). With the decreasing of $\Delta(\delta^{13}\text{C}_2-\delta^{13}\text{C}_1)$, $\delta^{13}\text{C}_2$ becomes lighter and gradually changes from coal-type gas into oil-type gas. Furthermore, $\Delta(\delta^{13}\text{C}_2-\delta^{13}\text{C}_1) = 5$ divides the natural gas into highly mature gas (the upper part) and over-mature gas (the lower part). The $\Delta(\delta^{13}\text{C}_2-\delta^{13}\text{C}_1) = 0$ subdivides the over-mature gas zone into three regions, namely the over-mature positive-sequence oil-type gas, over-mature positive-sequence coal-type gas, and over-mature reverse-sequence oil-type gas. Obviously, with the help of this chart, coal-type gas can be easily differentiated from oil-type gas, and the C-P natural gas in the Upper Paleozoic presents the characteristics of highly mature positive-sequence coal-type gas. The Cambrian gas is mainly over-mature reverse-sequence oil-type gas, with one sample showing the characteristic of highly mature positive-sequence coal-type gas. The reverse sequence of carbon isotope in Cambrian gas may be caused by the oil cracking in the over-mature stage. The origins of the weathered crust gas and pre-salt gas are relatively complicated. The weathered crust gas mainly manifests itself as highly mature positive-sequence coal-type gas, whereas some present themselves as highly mature positive-sequence

oil-type gas and over-mature reverse-sequence oil-type gas. The reverse-sequence oil-type gas may be caused by mixing of natural gas with different thermal evolution degrees or origins. Moreover, the pre-salt gas is mainly seen as high-over mature positive-sequence oil-type gas, and yet a few are displayed as highly mature positive-sequence coal-type gas. The origin of the western margin gas is relatively simple, mainly identified as high-over mature positive-sequence oil-type gas. The Ordovician deep gas is characterized by coexisting of gas of different origins, that is, some identified as highly mature positive-sequence coal-type gas and some classified as high-over mature positive-sequence oil-type gas. Combined with the planar distribution characteristics of the Lower Paleozoic source rocks [12], it is easy to conclude that coal-type gas is mainly distributed in the northwestern of the Sulige gas field, oil-type gas is mainly distributed in the western margin of the basin and in the southern of the basin, and mixed gas is primarily distributed in the Jingbian gas field and Ordovician pre-salt layers on the east of the Jingbian field.

4.3 Sources of natural gas

Affected by the structural background, especially the paleo-uplift, the natural gas sources of the Lower Paleozoic vary in different areas. Specifically, the development of the north-south-trending central paleo-uplift during the Ordovician

Figure 6: Scatter plot of $\delta^{13}\text{C}_2$ and $\Delta(\delta^{13}\text{C}_2-\delta^{13}\text{C}_1)$ of natural gas in the Lower Paleozoic of Ordos basin.

sedimentation resulted in certain differences in natural gas sources between the western margin and the mid-eastern part of the basin. During the Ordovician sedimentation, “L”-shaped marine troughs developed in the western and southern margins of the basin [11]. The Carbon isotopes of methane and ethane of the western margin gas are -38.9 to -35.6‰ and -35.9 to -27.2‰ , respectively, which indicate the natural gas are mainly high-over mature oil-type gas. Its isotopes are obviously different from the natural gas generated by the overlying Carboniferous Permian source rocks. In Ordovician strata, only O_2w and O_1k marine source rocks have a relatively high hydrocarbon generation potential [23]. For instance, Well Z4 obtained an industrial gas stream at $42,000 \text{ m}^3/\text{days}$ from the O_2w formation. Therefore, the western margin gas may mainly come from the marine source rocks of O_2w and O_1k marine source rocks and thus self-generating and self-storing gas reservoirs tend to occur (Figure 7).

The ethane carbon isotopes of the mostly pre-salt gas in mid-eastern part is less than -30.0‰ , which indicate the natural gas are mainly high-over mature oil-type gas, among which some of the reverse-sequence oil-type gas is presumed to be attributed to mixing of natural gas with different maturities. According to the gas accumulation mode in the Ordovician system shown in Figure 7, it is clear that in the mid-eastern basin, source rock develops

in the pre-salt Majiagou formation, there are three areas with well-developed source rocks, large thickness, and high organic carbon content [24]. As the pre-salt strata have a long vertical distance to the C–P coal-measure source rock, it would be difficult for the natural gas generated by the coal-measure source rock to migrate downward into the pre-salt reservoirs and accumulate at a large scale. Therefore, the oil-type gas in the pre-salt strata in the Middle East of the Ordos basin mainly comes from the marine source rocks developed in the Majiagou formation. In addition, a few of them have obvious characteristics of high mature coal-type gas, and their ethane carbon isotope is heavier than -26.0‰ , which is similar to the characteristics of Upper Paleozoic coal-type gas. However, influenced by the Caledonian orogeny, a regional unconformity developed at the top of the Ordovician system, which makes the C–P coal-measure source rock directly contact with the pre-salt strata near the central paleo-uplift. After the structural inversion of the Yanshanian period, the eastern part was uplifted, and the C–P coal-type gas was likely to migrate into and accumulate at the pre-salt strata.

The Ordovician deep (Ma_3 – Ma_4 members) gas in the mid-eastern part is complex, as some are oil-type gas with high-over maturity with the ethane isotope lighter than -29.0‰ , and positive sequence and others are coal-type

Figure 7: The accumulation mode of the Ordovician Natural Gas, the Ordos basin (the profile location is shown in Figure 1).

gas with the ethane isotope heavier than -26.5‰ . It is obvious that the oil-type gas is from the O_{1m} marine source rocks [24], and what seemed to be a puzzle is how the highly mature coal-type gas migrated to the Ordovician deep Ma_3 – Ma_4 members. After all, between the Ma_3 – Ma_4 members and the Upper Paleozoic C–P coal-measure source rock in the central-eastern parts deposits the nearly 400 m-thick Ma_5 member with interbed of dolomite, limestone, mudstone, and gypsum-salt strata. The Ordovician natural gas accumulation modes for the western margin, the central paleo-uplift, and the mid-eastern part are different (Figure 7). It can be reflected clearly that the C–P coal-measure source rock directly contacts with the Ma_4 Member or the pre-salt strata in the well DT1 near the central paleo-uplift, which allows the C–P coal-type gas to migrate into the pre-salt Ordovician strata or deeper Ma_3 – Ma_4 members in the central-eastern parts. However, the hydrocarbon-generated salt depressions of the O_{1m} are mainly distributed in the mid-eastern basin, and the farther east, the more gypsum-salt, salt rock, limestone, and mudstone [11,12]. The coal-type gas in the Upper Paleozoic migrated eastward after entering the pre-salt strata or the Ordovician Ma_4 member via the vicinity of DT1, then was blocked by tight rock barriers (such as gypsum-salt rock, limestone or mudstone) in the east,

and finally moved downward into and accumulated at the Ma_3 – Ma_4 members via faults.

The unconformity at the top of the Ordovician leads to the C–P coal-measure source rocks directly contacting with the weathered crust reservoir at the top of the Majiagou formation in a large scale; therefore, it is believed that the weathered crust gas with the ethane isotope heavier than -26.5‰ in the mid-eastern parts mainly comes from the C–P coal-measure source rocks, whereas small portion with the ethane isotope lighter than -28.5‰ are oil-type gas from the O_{1m} marine source rocks, this strata are considered to be an effective source rock [24].

The Cambrian gas is mainly distributed in the Qingyang area, where the long-term paleo-uplift, the Qingyang paleo-uplift (Figure 1) makes the Upper Paleozoic strata directly contact with the Majiagou formation and even the Cambrian system. Therefore, some scholars believed that the Cambrian gas in this area mainly comes from the C–P coal-measure source rocks [25]. However, the analysis of the natural gas genesis shows that the Cambrian gas is dominated by over-mature reverse-sequence oil-type gas with the ethane isotope lighter than -36.0‰ , with one sample showing highly mature positive-sequence coal-type gas, and such results are consistent with the viewpoint that the gas generation potential of Upper Paleozoic C–P coal-measure

Figure 8: The accumulation mode in the Cambrian natural gas of the southern Ordos basin (the profile location is shown in Figure 1).

source rocks are relative low in the Qingyang area [11]. In addition, high-abundance marine source rocks of the Lower Cambrian Luoquan-Dongpo formations [10,12] and marine source rocks of the Middle Ordovician Pingliang formation relatively extensively deposited in the southern basin, both with large hydrocarbon generation potential [12]. Before the Indosinian orogeny, the southern of Ordos basin was a simple south-dipping slope structure. Such a structural background makes it possible for natural gas generated by marine source rocks in the Cambrian and Ordovician systems migrated toward and accumulated at the Qingyang paleo-uplift in the southern basin (Figure 8).

5 Conclusion

The different origins and sources of natural gas lead to the difference of natural gas accumulation modes in the Lower Paleozoic of the Ordos basin. The accumulation mode in the western margin gas is relatively simple, and the gas is mainly oil-type gas from the O_1k and O_2w source rocks, suggesting the self-generating and self-storing gas reservoirs. Affected by the regional unconformity and the central paleo-uplift, accumulation of the Ordovician natural gas in the mid-eastern part is more complicated than that in the western margin of the basin. Presence of unconformity resulted in the weathered crust gas in the mid-eastern region, composed of the primary portion the C–P coal-measure source rocks and secondary portion from the O_1m marine source rocks. Moreover, part of the Ordovician deep gas in the mid-eastern basin appears as oil-type, and which comes from the O_1m marine source rock. Due to the joint effects of unconformity and faults, part of the coal-type gas generated by C–P source rock, first, move eastward through the unconformity near the central paleo-uplift, and then migrated downward along the fault and accumulated in Ordovician deep Ma_3 – Ma_4 strata after meeting barriers of the pre-salt gypsum salt rocks. In contrast, the pre-salt gas in the mid-eastern basin is mainly oil-type gas from the O_1m source rocks. The Cambrian gas mainly comes from the Cambrian or Ordovician marine source rocks in the southern basin.

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References

- [1] Dai JX, Li J, Luo X, Zhang WZ, Hu GY, Ma CH, et al. Stable carbon isotope compositions and source rock geochemistry of the giant gas accumulations in the Ordos Basin, China. *Org Geochem.* 2005;36(12):1617–35.
- [2] Stahl WJ. Carbon and nitrogen isotopes in hydrocarbon research and exploration. *Chem Geol.* 1977;20:121–49.
- [3] Berner U, Faber E. Maturity related mixing model for methane, ethane and propane, based on carbon isotopes. *Org Geochem.* 1988;13:67–72.
- [4] Zhang W, Pei G, Guan D. Carbon isotopic distribution characteristics of light hydrocarbon monomeric series of crude oils in the Ordos Basin. *Chinese Sci Bull.* 1993;38(1):64–8.
- [5] Xia XY, Dai JX. A critical review on the evaluation of hydrocarbon potential of marine carbonate rocks in China. *Acta Petrolei Sin.* 2000;21(4):36–41 (in Chinese with English abstract).
- [6] Cai CF, Hu GY, He H, Li J, Li JF, Wu YS. Geochemical characteristics and origin of natural gas and thermochemical sulphate reduction in Ordovician carbonates in the Ordos Basin, China. *J Pet Sci Eng.* 2005;48(3–4):209–26.
- [7] Chen AD. Origin and migration of natural gas in Ordovician reservoir in Ordos Basin Central Gas Field. *Acta Petrolei Sin.* 1994;15(2):1–10 (in Chinese with English abstract).
- [8] Liu QY, Chen MJ, Liu WH, Li J, Han PL, Guo YR. Origin of natural gas from the Ordovician paleo-weathering crust and gas-filling

- model in Jingbian gas field, Ordos Basin, China. *J Asian Earth Sci.* 2009;35:74–88.
- [9] Kong QF, Zhang WZ, Li JF, Zan CL. Geochemical characteristics and genesis of Ordovician natural gas under gypsolyte in Ordos Basin. *Nat Gas Geosci.* 2019;30(3):423–32 (in Chinese with English abstract).
- [10] Huang JP, Li XB, He WX, Wanyan R, Bao HP, Xu YH, et al. Formation Environment and Development Models for the Lower Cambrian Source Rocks of the Southern North China Plate, China. *ACS OMEGA.* 2020;5:8001–11.
- [11] Yang H, Liu XS, Zhang DF. Main controlling factors of gas pooling in Ordovician marine carbonate reservoirs in the Ordos Basin and advances in gas exploration. *Nat Gas Ind.* 2013;33(5):1–12 (in Chinese with English abstract).
- [12] Du JH, Li XB, Bao HP, Xu WL, Wang YT, Huang JP, et al. Geological conditions of natural gas accumulation and new exploration areas in the Mesoproterozoic to Lower Paleozoic of Ordos Basin. *NW China Pet Explor Dev.* 2019;46(5):866–82.
- [13] Han WX, Chang XC, Tao SZ, Hou LH, Ma WJ, Yao JL, et al. Geochemical characteristics and genesis of pre-salt gases in the Ordos Basin. *China J Pet Sci Eng.* 2019;179:92–103.
- [14] Prinzhofer A, Huc AY. Genetic and post-genetic molecular and isotopic fractionations in natural gases. *Chem Geol.* 1995;126(3–4):281–90.
- [15] Burruss RC, Laughrey CD. Carbon and hydrogen isotopic reversals in deep basin gas: evidence for limits to the stability of hydrocarbons. *Org Geochem.* 2010;41:1285–96.
- [16] Tilley B, McLellan S, Hiebert S, Quarero B, Veilleux B, Muehlenbachs K. Gas isotope reversals in fractured gas reservoirs of the western Canadian Foothills: mature shale gases in disguise. *AAPG Bull.* 2011;95(8):1399–422.
- [17] Tilley B, Muehlenbachs K. Isotope reversals and universal stages and trends of gas maturation in sealed, self-contained petroleum systems. *Chem Geol.* 2013;339:194–204.
- [18] Zumberge J, Ferworn K, Brown S. Isotopic reversal ('rollover') in shale gases produced from the Mississippian Barnett and Fayetteville formations. *Mar Pet Geol.* 2012;31(1):43–52.
- [19] Huang DF, Xiong CW, Yang JJ, Xu ZQ, Wang KR. Gas source discrimination and natural gas genetic types of central gas field in Erduosi Basin. *Nat Gas Ind.* 1996;16(6):1–5 (in Chinese with English abstract).
- [20] Dai JX. Identification and distinction of various alkane gases. *Sci China Ser B.* 1992;35:1246–57 (in Chinese with English abstract).
- [21] Wang FY, Tang YC, He ZY, Li JK, Zhen HS. Map based isotopic kinetical tool to simulate the generation and accumulation history of natural gas. New Orleans, Louisiana: AAPG Annual Convention and Exhibition; April 11–14, 2010.
- [22] Dai JX, Gong DY, Ni YY, Huang SP, Wu W. Stable carbon isotopes of coal derived gases sourced from the Mesozoic coal measures in China. *Org Geochem.* 2014;74:123–42.
- [23] Zhang YQ, Guo YR, Hou W, Zhao ZY, Gao JR. Geochemical characteristics and exploration potential of the Middle-Upper Ordovician source rocks on the western and southern margin of Ordos Basin. *Nat Gas Geosci.* 2013;24(5):894–904.
- [24] Yao JL, Wang CC, Chen JP, Gao G, Wang YF, Li XF, et al. Distribution characteristics of sub-salt carbonate source rocks in Majiagou formation. *Ordos Basin Nat Gas Geosci.* 2016;27(12):2115–26.
- [25] Fu JH, Wei XS, Luo SS, Zuo ZF, Zhou H, Liu BX, et al. Discovery and geological knowledge of the large deep coal-formed Qingyang Gas Field, Ordos Basin, NW China. *Pet Explor Dev.* 2019;46(6):1111–26.