Geochemical characteristics and significance of the bitumen in Sinian reservoirs in Sichuan basin and its periphery

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Abstract: The bitumen of Doushantuo Formation distributed along fractures has been firstly discovered in the dolomite reservoirs of Dou-3 Member in Zigui region, Yichang, Hubei. Research has been conducted using multiple methods on the characteristics of the newly discovered bitumen of Doushantuo Formation, bitumen of Dengying Formation-Longwangmiao Formation in Anyue gas field in Sichuan Basin, and bitumen of Sinian and source rocks of Sinian-Cambrian in Northeast Sichuan. The results show: \textsuperscript{1} The reflectivity of the bitumen of Dou-3 Member is about 2.8\%; \textsuperscript{2} The carbon number of n-alkanes in the bitumen of Dou-3 Member is C\textsubscript{13}-C\textsubscript{33}, where nC\textsubscript{17} is the main peak; the relative proportion of the regular steranes is C\textsubscript{27}≈C\textsubscript{29}>C\textsubscript{28}, and C\textsubscript{27}, C\textsubscript{28} and C\textsubscript{29}ααα20R steranes are distributed in "L" shape; abundant tricyclic terpanes and pentacyclic triterpanes have been detected, and the abundance of gammacerane is high; Aromatics are mainly phenanthrene series compounds. \textsuperscript{3} The heteroatomic compounds in the bitumen of Dou-3 Member are mainly O2 carboxylic acids, and the oxygen compounds in the bitumen of Dengying Formation in Anyue gas field are close to those of the source rocks of Doushantuo Formation. The research results are of vital guiding significance to the study of potential source rocks of Doushantuo Formation in Sichuan Basin and the exploration of oil and gas from the source rocks of Doushantuo Formation.

1. Introduction

The black mud shales of Doushantuo Formation are developed to a very high degree in the Yangtze region, and are good source rocks and also one of the most important source rock series of strata of Neoproterozoic Sinian in China. Field outcrops show that high-quality thick black mud shales of Doushantuo Formation are developed in Yichang, Hubei and Chengkou region, Northeast Sichuan. CGS Oil and Gas Resource Investigation Center also discovered the shale gas of Doushantuo Formation in wells ZD1 and EYY 1 deployed in Yichang, Hubei\textsuperscript{1,2}. Reservoir bitumen, as the residues after cracking of crude oil into gas, is a bridge for tracking and comparison of natural gas-source rocks in the study of deep high-maturated natural gas sources, but there are no relevant reports on the characteristics of liquid hydrocarbons (bitumen) from the source rocks of Doushantuo Formation. The
The author discovered the self-source and self-reservoir (i.e., source rock of Dou-2 Member and reservoir of Dou-3 Member) bitumen of Doushantuo Formation distributed along fractures in the dolomite reservoir of Dou-3 Member in Luojia Village, Yichang, Hubei for the first time. In addition, the author has studied the characteristics of the newly discovered bitumen of Doushantuo Formation using the analysis methods such as geochemistry, organic petrology, etc. combined with the advanced Fourier transform ion cyclotron resonance mass spectrometry (FT-ICRMS) analysis technology. Moreover, the characteristics of the newly discovered bitumen have been compared with the characteristics of the Sinian-Cambrian bitumen and source rocks in Sichuan Basin and its periphery. This is of vital significance to the research on ascertaining whether the source rocks of Doushantuo Formation contribute to the overlying reservoirs etc.

2. Geologic background

In the early Neoproterozoic (900-700 Ma), with the disintegration of the global Rodinia supercontinent, the ancient land of South China also began to disintegrate accordingly. Subsequently, two global glacial events occurred during the Nanhua Period: the Sturt Glacial Period of about 720 Ma and the Marino Glacial Period of 635 Ma. After the two glacial periods, two sets of organic-rich source series of strata such as Datangpo Formation and Doushantuo Formation were deposited in South China. The outstanding feature of Doushantuo Formation in Sichuan Basin and its periphery is that the Formation directly overlies the Nantuo moraine pebbly sandstones. Doushantuo Formation can be divided into four lithologic members from bottom to top in Yichang, Hubei, Chengkou region, Chongqing, etc. The lithology of Dou-2 Member and Dou-4 Member is mainly argillaceous rocks, which are the earliest source series of strata developed after the tillite of Nantuo Formation. The lithology of Dou-3 Member includes dolomites and argillaceous siltstones, which are mainly reservoirs. There are certain differences in the paleoenvironment during the deposition period of Doushantuo Formation; during the deposition of the source rocks of Doushantuo Formation in Northeast Sichuan, the hydrodynamic force was weak, the salinity was low, and the paleoenvironment was an oxygen-deficient deep-water shelf environment, while during the deposition of Doushantuo Formation in Western Hubei, the hydrodynamic force was strong, the salinity was low, and the paleoenvironment was an oxygen-deficient intra-platform basin environment. The Doushantuo Formation in Luojaucun Section, Zigui, Yichang, Hubei is about 170m thick (Figure 1), and the main intervals of source rocks are Dou-2 Member and Dou-4 Member. The thickness of Dou-2 Member is about 100~120m, and that of Dou-4 Member is 10-15m. The TOC of mudstones is mainly 1%~2.5%, the organic matter type is I-II1, and the equivalent vitrinite reflectance Ro is 1.8%~2.2%.

3. Experimental samples

The field samples collected in this study came from the source rocks of Doushantuo Formation in Luojiacun Section, the bitumen in the dolomite reservoirs of Dou-3 Member (Figure 1), the source rocks of Doushantuo Formation in Zhong'an Village, Chengkou, Chongqing, and the bitumen of Dengying Formation in Muhuaihe and Chafengcun Section; the downhole samples were mainly from the bitumen of Longwangmiao Formation in well LT1 etc. and the bitumen of Dengying Formation in well MX8 etc. in Anyue gas field in Central Sichuan. The sampling locations are shown in Figure 1.
Figure 1. Location of study area and profile of Doushantuo Formation in Yichang (Nanhua system rift according to Ref.\cite{7})

4. Results and Discussion

4.1 Characteristics of saturated hydrocarbon n-alkanes
The distribution of reservoir bitumen n-alkanes in Doushantuo Formation is normal, and the bitumen belongs to the residual bitumen after crude oil cracking. The reflectivity of the bitumen is 2.52\%~2.97\%, with an average of 2.8\%; the carbon number of n-alkanes is nC\textsubscript{13}~nC\textsubscript{33}, and the main peak is nC\textsubscript{17}; the Pr/Ph ratio is 0.60~0.63.

4.2 Characteristics of steranes and terpanes
Abundant tricyclic terpane series compounds and pentacyclic triterpane series compounds have been detected in the reservoir bitumen and source rocks in Doushantuo Formation (Figure 2). The carbon number C\textsubscript{19}~C\textsubscript{29} of tricyclic terpanes is complete, dominated by C\textsubscript{23} tricyclic terpanes; in addition, the C\textsubscript{21}/C\textsubscript{23} ratio of 0.65~0.66, which is similar to that of the source rocks of Dou-2 Member. Among the pentacyclic triterpane series compounds, C\textsubscript{30} hopane is the main compound, and the abundance of gammacerane is high; in addition, the abundance of C\textsubscript{31}~C\textsubscript{35} homohopanes gradually decreases as the carbon number increases, and the ratio of tricyclic terpane/hopane is 0.27~0.32, which is similar to that of the source rocks of Doushantuo Formation. The ratio of gammacerane/C\textsubscript{31} homohopane is 0.60~0.69; the homohopane index (C\textsubscript{31,35}/C\textsubscript{30}) is 0.64~0.65; T\textsubscript{5}/Tm is 0.82~0.96.
Abundant sterane series compounds have been detected in the reservoir bitumen in Doushantuo Formation (Figure 3). $C_{27}$, $C_{28}$, and $C_{29}$ regular steranes are abundant, their relative ratio is $C_{27} > C_{29} > C_{28}$, and the sterane abundance composed of $C_{27}$, $C_{28}$, and $C_{29}^{20R}$ is distributed in "L" shape, similar to the characteristics of the source rocks in Doushantuo Formation, which reveals that the main sources are bacteria and algae. In addition, they all contain a certain abundance of pregnane, homopregnane and rearrangement sterane.

Figure 4 shows that the bitumen in Doushantuo Formation has similar sterane distribution characteristics to the shales in Yichang Doushantuo Formation and the mudstones in Chengkou Doushantuo Formation, indicating that the bitumen in the dolomite reservoirs of Dou-3 Member comes from the source rocks of Doushantuo Formation; The bitumen of Gaomo Dengying Formation is also dominated by $C_{29}$ steranes, while the bitumen and source rocks of Cambrian are dominated by $C_{27}$ steranes relative to Sinian.
4.3 Characteristics of aromatic compounds

Among the aromatic compounds of the reservoir bitumen in Doushantuo Formation, phenanthrene series compounds predominate (Figure 5), accounting for 33.5%~38.5%, followed by naphthalene series compounds, accounting for 20.9%~21.9%; dibenzothiophene series, benzofuran series and fluorene series compounds account for 4.3%~12.9%, 4.7%~5.0%, and 4.4%~5.7% respectively; the abundance of triaromatic steroid series compounds is low, accounting for only 0.8%~1.1%. The characteristics of aromatic compounds of bitumen in Dou-3 Member are similar to those of source rocks in Doushantuo Formation.

4.4 Characteristics of NSO heteroatomic compounds

FT-ICRMS has ultra-high precision and significant advantages in the analysis of NSO heteroatomic compounds. The heteroatomic compounds detected by FT-ICRMS in ESI negative ionization are mainly alkaline nitrogen compounds and acidic compounds such as naphthenic acids and phenols etc.\cite{9,10}.
4.4.1 Type of compounds and their relative abundance

The tests of detection by FT-ICRMS in ESI negative ionization show that the composition of heteroatomic compounds in the bitumen and source rocks of Doushantuo Formation and the bitumen of Dengying Formation-Longwangmiao Formation is very complex. According to the different number of N and O heteroatoms in molecules, totally 7 compounds with different heteroatom types have been identified: N1, N1O1, N1O2, O1, O2, O3, and O4 compounds, of which O2 compounds predominate (Figure 6). The bitumen of Doushantuo Formation, the source rocks of Doushantuo Formation, and the bitumen of Dengying Formation and Longwangmiao Formation are all dominated by O2 compounds, but the relative content of other compounds except O2 compounds in Longwangmiao Formation is relatively low, and the bitumen of Dengying Formation and the source rocks of Doushantuo Formation contain a certain amount of O3 and O4 compounds. The relative content of O2 and O3 compounds in the bitumen of Doushantuo Formation, Dengying Formation and Longwangmiao Formation is different (Figure 7).

![Figure 6. Relative abundance of different compounds in ESI negative ionization, FT-ICRMS](image)

![Figure 7. Relative content distribution of oxygen compounds in ESI ionization, FT-ICRMS](image)

4.4.2 Characteristics of O2 compounds
A compound containing two oxygen atoms in the molecule may be carboxylic acid or diatomic alcohol. Ethers and ketones are difficult to ionize in ESI negative ionization, so O2 compounds contain at least one hydroxyl group. According to the minimum degree of condensation DBE (Double Bond Equivalent) of diatomic alcohols and the minimum DBE of O2 in source rocks and bitumen, it is inferred that O2 compounds are mainly carboxylic acids[11,12]. The DBE statistics of O2 compounds show that the main peak of the O2 compounds in the bitumen of Longwangmiao Formation is 2DBE, and the DBE=2-6 are dominated by naphthenic acids; the main peak of the O2 compounds in the source rocks and bitumen of Doushantuo Formation and the reservoir bitumen of Deng-2 Member is 1DBE; the bitumen of Deng-4 Member has some 1DBE main peaks and 2DBE main peaks (Figure 8). The bitumen of Longwangmiao Formation is significantly different from the source rocks of Doushantuo Formation, while Deng-2 Member close to Doushantuo Formation is similar to the source rocks of Doushantuo Formation, and Deng-4 Member lies between the bitumen of Longwangmiao Formation and the source rocks of Doushantuo Formation.

Figure 8. DBE peak distribution of O2 compounds from ESI negative ionization, FT-ICRMS

Previous studies have shown that Nanhua rifts are developed in Central Sichuan[7,13-15], and have laid a favorable geological foundation for the development of the source rocks of the overlying Doushantuo Formation. Therefore, it is possible to find paleo-reservoir pyrolysis gas from the source rocks of Doushantuo Formation in Sichuan Basin.

5. Conclusions
(1) The reservoir bitumen of Doushantuo Formation belongs to the residual bitumen after crude oil cracking. The reflectivity of the bitumen is about 2.8%, which is in the post-mature stage, and has the Pr/Ph of 0.60~0.63, reflecting a strong reducing environment during the deposition of the source rocks in Doushantuo Formation.

(2) Abundant tricyclic terpane series compounds and pentacyclic triterpane series compounds have been detected in the reservoir bitumen of Doushantuo Formation. C27, C28 and C29 regular steranes are abundant in sterane series compounds, and C27, C28 and C29ααα20R steranes are distributed in "L" shape. Among the aromatic compounds, phenanthrene series compounds predominate, and their biomarker characteristics show that they are similar to the source rocks of Doushantuo Formation.

(3) The results of detection by FT-ICRMS in negative ionization show that the acidic heteroatomic compounds in the bitumen of Doushantuo Formation are mainly O2 carboxylic acid compounds, and fatty acid compounds (DBE=1) have a strong even-carbon advantage, similar to the source rocks of Doushantuo Formation.
(4) The bitumen of Dengying Formation in Anyue gas field has similar characteristics to the bitumen of Doushantuo Formation. The Nanhua rifts in Central Sichuan have established favorable conditions for the development of source rocks of Doushantuo Formation, and are of vital significance to the research on the evaluation of the contribution of source rocks of Doushantuo Formation to Dengying Formation gas reservoirs.

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