Deep and Ultra-deep oil/gas-source correlation methods: A review

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Abstract. With the deepening of oil and gas exploration practice, the increasing degree of oil and gas exploration and the increasing demand for oil and gas, the target of oil and gas exploration is gradually transformed into deep and ultra-deep areas. Meanwhile, the genesis of deep and ultra-deep reservoirs has gradually become the focus of research by domestic and foreign scholars. Oil/gas source correlation is an important means to study the genetic relationship between oil and gas and source rocks. Based on the geological and geochemical data, this paper summarizes and analyzes the advantages and disadvantages of the current methods of deep and ultra-deep oil/gas source correlation, and puts forward the existing problems and future development direction of deep and ultra-deep oil/gas source correlation.

1. Introduction

With the increasing difficulty in finding large oil and gas reservoirs in the middle and shallow strata, oil and gas exploration has been extended to the deep and ultra-deep regions all over the world [1]. Compared with the middle and shallow reservoirs, the deep and ultra-deep reservoirs are not only difficult and expensive to explore, but also have complex geological characteristics, special hydrocarbon genesis and accumulation modes [2,3]. Therefore, there are still numerous challenges in the exploitation of deep and ultra-deep reservoirs. At present, the source rocks, types of hydrocarbon properties, and accumulation models of deep and ultra-deep reservoirs are the focus of scholars at home and abroad. However, there is a lack of systematic research on the genesis, distribution and source correlation of deep hydrocarbon.

Comparing kerogen, bitumen, condensate, and natural gas with appropriate indexes is an important way to reveal the source of oil and gas, the genetic relationship between source rock and natural gas, and the availability of source rock, which is of great significance to the development and exploration of deep and ultra-deep oil and gas fields. However, it is necessary to consider the effects of biodegradation, maturity, migration and water washing on chemical composition of crude oil comprehensively when comparing oil and gas sources.

At present, the deep and ultra-deep source rocks summarized by domestic and foreign scholars have the following characteristics [4]. (1) The maturity and thermal evolution of organic matter are relatively high. (2) The types of organic matter are different: on the one hand, the lacustrine source rocks in the eastern basin are mostly terrigenous clastic shale, and most of the natural gas has the characteristics of direct kerogen gas generation; on the other hand, the organic matter of marine source rocks in the central...
and western basins is dominated by sapropelic organic matter. In addition to kerogen gas, natural gas also has been formed by palaeo-petroleum cracking. (3) The total organic carbon (TOC) is different: the TOC content of lacustrine source rocks in the eastern basin is relatively high, mostly not less than 5%, while the TOC of marine source rocks in the central and western basins is relatively low, only above 0.5%[5]. (4) The development scale of marine source rocks is different from that of lacustrine source rocks. (5) In addition to being affected by temperature and time, hydrocarbon generation is also be affected by high pressure[6]. These characteristics determine the above characteristics and non-genetic factors, especially the degree of thermal evolution, should be considered comprehensively when selecting appropriate oil source comparison parameters in the study of deep and ultra-deep oil source. And the principles are as follows: (1) Perform multi-feature detection on samples and obtain evidence indicating the origin of oil and gas. (2) Try to use samples with less epigenetic and secondary changes. (3) Use source rock samples with appropriate maturity and avoid using immature and over-mature samples. (4) In order to reduce the interference of secondary factors, the absolute concentration of organic compounds should be used as little as possible, and the distribution pattern and relative ratio of the series of compounds should be used. (5) Try to choose oil source comparison parameters that are not controlled by maturity.

2. Oil/gas source correlation methods currently used in deep and ultra-deep source rocks

2.1. Biomarker related methods

2.1.1. Comprehensive comparison method of multi-factors biomarker compound parameters

When there is a relationship between source rocks and crude oil, their chemical composition is similar and they show similar spectral characteristics in the spectrum, which can be used as a basis for identification. The advantage of this approach is that it is more intuitive. However, because the oil is buried more deeper, it is easy to be affected by secondary action, and the physical and chemical properties of crude oil have changed greatly in the later stage. Moreover, the maturity of deep-ultra-deep crude oil is relatively high, which is generally in the high over-mature stage. The content of soluble organic matter in source rock is low, and it is easy to be affected by later migration and pollution hydrocarbon. Biomarkers may also be transformed by thermal action and lose their original distribution characteristics, so they cannot be used for accurate oil source correlation, and it's even more difficult to be identified directly on the spectrogram. Considering the limitation of a single indicator, most of the current studies use the multi-factors biomarker parameters comprehensive comparison method to comprehensively analyze multiple biomarker parameters, so as to make the comparison results more accurate. The main parameters of biomarkers include light hydrocarbon index, aromatics index, steranes and terpenes biomarkers index, isoprenoid alkanes index, etc[7], the relative strength of several specific indicators of crude oil and source rock is plotted as a correlation curve, through which the parent-source relationship between crude oil and source rock can be judged. Or the relative content of biomarkers can be normalized and then drawn into triangular and other correlation diagrams. Finally, comparisons can be made according to various correlation diagrams. These methods are more commonly used comprehensive methods[8].

Deep and super-deep oil and gas are characterized by multi-source, multi-stage accumulation, high temperature and high pressure, low porosity and permeability, and strong reduction environment, etc. The complexity caused by factors such as maturity, migration, PVT conditions and biodegradation must be fully considered in the identification of oil source relationship. The oil source correlation parameters which are less affected by maturity are mainly considered, such as isoprenoid alkanes [9], macro composition of aromatic compounds, etc[10].

2.1.2. ruthenium ion catalytic oxidation (RICO)

In addition to selecting the biomarker compound oil source comparison parameters that are not affected by non-generating factors, it is also a better method to try to restore the accurate information about the biomarkers in crude oil. As a highly selective and mild chemical degradation method, the ruthenium ion catalytic oxidation (RICO) of asphaltene is the most important method for identifying the source of
crude oil which was severely biodegraded\textsuperscript{[11,12]}. The biomarkers bound in asphaltenes can be obtained by using RICO chemical degradation method, which can "restore" the original free state of the biological compounds. Moreover, it can be used to compare the types of sedimentary parent materials, biological sources and oil sources. This method has the practical value to study the correlation between biodegraded crude oil and source rocks\textsuperscript{[13]}. Ma et al.\textsuperscript{[9]} used asphaltene ruthenium ion catalytic oxidation technology to study the sources of the Lunnan and Tahe heavy oil in the Tarim Basin. The results showed that the heavy oil in Lunnan, Tahe was different from the crude oil in Cambrian TD2 well, and it came from the Middle-Upper Ordovician source rocks.

Although the RICO method can provide some information on the initial characteristics of crude oil, the biomarker information may be changed after the crude oil is chemically treated due to the secondary cracking of chemical bonds in the progress of RICO. Some scholars suggested that the complex three-dimensional macromolecular network structure in asphaltenes, which can encapsulate other hydrocarbon components in the preservation environment and is difficult to be destroyed by organisms, can be used to restore the biomarker information of crude oil\textsuperscript{[14]}.

2.2. Isotope method

2.2.1. Carbon isotope method

The stable carbon isotope method is more important in the comparison of deep and ultra-deep oil sources, and has unique advantages as a parameter in the comparison of deep and ultra deep oil source. A large number of research results show that the carbon isotopic value of crude oil is mainly controlled by the organic carbon isotope composition of source rock\textsuperscript{[15]}. The influence of thermal evolution on the carbon isotopes of crude oil is relatively small and the variation of the carbon isotopes of crude oil is generally less than 2‰ during thermal evolution\textsuperscript{[16]}. Therefore, it is generally believed that it is more accurate to use the carbon isotope of crude oil as a parameter for deep source rock to do oil/gas-source correlation. When the source rock is the same, the environmental conditions and maturity are similar, the variation rule of isotope value in crude oil, kerogen, extract, and its components is: saturated hydrocarbon < crude oil < aromatic hydrocarbon < non hydrocarbon < asphaltene < kerogen. But it is difficult to identify the deviation degree of carbon isotope in oil source correlation due to the fractionation effect of carbon isotope.

2.2.2. Sulfur isotopes

Some deep and ultra-deep source rocks generated hydrocarbon and cracked oil in a relatively closed and rapid burial system. The crude oil and reservoir bitumen have not been reduced and transformed by thermochemical sulfate reduction (TSR) or bacterial sulphate reduction (BSR). As a result, the source of oil and gas can be determined by comparing their isotopic composition of organic sulfur in bitumen and crude oil or gas\textsuperscript{[17]}. Cai's team\textsuperscript{[18–20]} measured the molecular composition, the $\delta^{13}$C values of n-alkanes and the $\delta^{34}$S values of monoalkyl dibenzothiophene of potential source rocks and crude oils from Cambrian and Ordovician reservoirs to determine the source of crude oil. They had also explored whether the $\delta^{13}$C and $\delta^{34}$S values can be effectively used in comparative study of oil and gas sources. The sulfur isotope correlation results showed that the sulfur isotope of kerogen in Cambrian source rocks was similar to that of total sulfur isotope of crude oil which has not been degraded. Therefore, it is considered that the crude oil in Tarim Basin mainly came from Cambrian source rocks. At the same time, the study found that due to TSR, the $\delta^{13}$C and $\delta^{34}$S values of the Cambrian crude oil of ZS1C shifted to the corrected value.

Many deep oil/gas fields are characterized by high content of H$_2$S, and TSR is one of the sources of H$_2$S. The deviation of $\delta^{34}$S and $\delta^{13}$C caused by TSR will produce deviations in the comparison of the isotope values of source rocks and oil and gas, leading to inaccurate results. Therefore, the isotope method is not suitable for the oil/gas source correlation of crude oil and natural gas which reformed by TSR.

2.3. Trace element method
The organic matter of source rocks contains a certain amount of trace elements, which can be used to compare with the content of trace elements in the generated oil/gas to determine its composition. As a parameter of oil source correlation, trace elements have the advantage that they are not easily been changed due to oil and gas migration, reservoir destruction, oxidation, and biodegradation. Jiao et al. studied the occurrence state, activation and migration rule of trace elements in crude oil, and analyzed the fingerprint of trace elements. The results showed that rare earth element and transition metals can be used to study oil-gas source under the complicated conditions of hydrocarbon accumulation and migration. However, the content of asphaltenes in crude oil will gradually decrease with the increase of crude oil maturity. Since trace elements are mainly combined with asphaltenes, the abundance of most trace elements will decrease with the increase of petroleum maturity, which will make it hard to analyze the content of trace elements.

At present, this method is seldom used in the related literature on oil/gas source correlation of deep or ultra-deep oilfields. The geochemical behavior of trace elements in the process of crude oil formation and migration is very complicated. Trace element composition is controlled by many factors in hydrocarbon-water-rock systems, and its application is not as extensive as that of isotopes and biomarkers. However, when the conventional synthesis methods of isotopes and biomarkers are uncertain, trace element parameters can be used as supplementary methods.

3. Problems and future development directions in deep and ultra-deep oil/gas source correlation

(1) Compared with shallow reservoirs, deep and ultra-deep reservoirs in China are characterized by complex genesis and multi-stage structural evolution. The crude oil in many developed reservoirs is mixed source oil, which will affect the source identification of deep and ultra-deep crude oil. At present, artificial ratio simulation experiments have been used to identify the hydrocarbon source composition of deep and super-deep mixed oils. For example, Ma et al. carried out the crude oil ratio experiment on typical Cambrian crude oil of well TD2 with heavy oil of well LN1 and Ordovician crude oil of well YW2 in 2004. As the crude oil content of TD2 well was 25%, the mixed source oil also showed the characteristics of Cambrian hydrocarbon source. It refuted the claim that the middle and Upper Ordovician crude oil was polluted by Cambrian crude oil. But first, the crude oil ratio experiment directly ignored the existence of crush oil, which came from three or even more sources. Secondly, under the current research level of deep and ultra-deep oil and gas reservoirs, it is very difficult to find suitable samples that are not doped with single source and are suitable for matching experiments and end members of carbon isotope analysis. As a result, it is difficult to accurately identify the mixed source oil-source relationship in deep or ultra-deep oil before finding a suitable end member.

(2) High content of H₂S is one of the most significant characteristics of components in ultra-deep oil and gas reservoirs. These H₂S are mainly derived from the pyrolysis of sulfide in kerogen or crude oil, bacterial or microbial sulfate reduction (BSR) and thermochemical reduction of sulfate (TSR). However, the values of δ¹³C and δ³⁴S of crude oils that have undergone TSR, such as ZS1 Cambrian crude oils, shift to more positive values. Therefore, it is likely that the isotopic parameter matching between source rock and crude oil is caused by TSR alteration rather than genetic relationship, which results in inaccurate oil source correlation. Some studies have shown that high concentration of H₂S (>5%) in ultra-deep natural gas can indicate the presence of TSR in the process of oil and gas formation, and the value of TSR in Yuanba 1 area is reaching 12% [25, 26]. Perhaps the feasibility of isotope index can be judged by the concentration of H₂S and CO₂. As a result, it is urgent to find new oil source correlation parameters which are not controlled by other conditions except the genesis.

4. Conclusions

In recent years, oil and gas exploration has been expanding to deep and ultra-deep layers, and a series of new understanding and progress have been made in many aspects, such as deep and ultra-deep oil and gas genesis, types, reservoir forming models and source rocks of oil and gas. In the study of oil
source correlation of deep and ultra-deep oil and gas reservoirs, multi-factors biomarker parameters comprehensive comparison method, isotope method, trace element method and other methods have been applied. Due to the special accumulation model, complex genesis and more geological tectonic activities of deep and ultra-deep reservoirs, there are some limitations in the selection of oil source correlation parameters. How to select the appropriate oil source correlation methods and parameters will become one of the important research directions of deep and ultra-deep reservoirs.

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