Geochemical studies on high-efficiency hydrocarbon expulsion of Triassic lacustrine shale in the Ordos Basin, China: implications for tight and shale oil accumulation

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Abstract. The organic-rich sediments developed at the bottom of Chang7 Member of the Upper Triassic Yanchang formation, which can be divided into oil shale and black mudstones, are dominate source rocks for low permeability and tight oil reservoirs in Mesozoic petroleum system of Ordos Basin. The hydrocarbon expulsion characteristics of the organic-rich sediments have been investigated by geology and geochemistry data. By comparison with the geochemical parameters of crude oil samples and mudstone extracts, Chang7 shale has many geochemical evidences on high rates of hydrocarbon expulsion. Lower conversion rate of chloroform extracted bitumen "A", especially for the samples with TOC higher than 10%; lower productivity indexes and lower hydrogen indexes reducing with TOC increasing; lower ratios of saturates/aromatics but higher contents of polar components for residual bitumen "A"; heavier stable carbon isotopes of residual hydrocarbons. It should be noted that the source rock evaluation and oil-source correlation would be misunderstood based on these abnormal geochemical data caused by high-efficiency hydrocarbon expulsion. Calculation for rock samples have shown that the expelled rates of the shale samples averaging 70% are significantly higher than those of the mudstone samples. Chang7 shale with large amounts of hydrocarbons generated and expelled is critical for hydrocarbon accumulation in low-permeability and tight oil reservoirs. Also, Chang7 organic-rich rocks is an important exploration field of shale oil in the future.

1. Introduction

Hydrocarbon expulsion, also called primary migration, which denotes the process of petroleum expelled from low permeability source rocks into more permeable carrier or reservoir rocks (Hunt, 1979; Tissot and Welte, 1984). It is one of the most essential studies in petroleum geology which fundamental for source rock evaluation and oil-source correlation. Also hydrocarbon expulsion characteristics and efficiencies would affect the amounts and compositions of expelled hydrocarbons. With the rise of shale oil and gas exploration in recent years, geologists and geochemists have attached more and more attention on efficiencies of primary migration and hydrocarbons remaining in the pore system of source rocks after petroleum expulsion. They have various viewpoints on hydrocarbon expulsion features. Some geochemists believed that the ratios of hydrocarbons expelled from, to generated in, shale source rocks were mainly controlled by kerogen quality (Eseme et al., 2007, 2012).
Zhang et al. (2006a) proposed that the kerogen richness had a positive relationship with the rates of hydrocarbon expulsion. Some other researchers suggested that kerogen maturity is another important factor for hydrocarbon expulsion, the higher the maturity, the more hydrocarbons were expelled (Pepper and Corvi, 1995; Cai et al., 2012). And some scholars found that thick source rocks were unfavorable for hydrocarbon primary migration, thus thin source rocks and the edge of thick source rocks usually expelled much more hydrocarbons (Leythaeuser et al., 1991; Zhao et al., 2006). In all, previous researches have shown that the efficiencies of primary migration may be controlled by kerogen richness, type and maturity, or source rock thickness and so on. The hydrocarbon generation and expulsion characteristics of source rocks are distinct under different geological conditions. In this paper, our topic is the lacustrine source rock in Ordos Basin, central China. Lots of literatures have been published on organic-rich rocks in Yanchang Formation of Ordos Basin, but only a few refers to hydrocarbon expulsion. Zhang et al. (2006a) have suggested that Chang 7 main source rocks have high rates of hydrocarbon expulsion, which is favorable for hydrocarbon accumulation in low-permeability reservoirs. Huang et al (2018) proposed that maturity and organic matter types are main factors for hydrocarbon expulsion, the rates of hydrocarbon expulsion range from 33%~67%. Our previous studies (Zhang et al, 2017; Yang et al., 2016) have revealed that Chang7 organic-rich sediments can be obviously classified into two categories including oil shale and black mudstone, and they vary in distribution, petrology, mineralogy and geochemistry resulting in distinct characteristics of hydrocarbon expulsion. Therefore, hydrocarbon expulsion needs more explanation and determination in order to discover the principal source rock. So far, the oil-source correlation of Mesozoic petroleum system in Ordos Basin is still misunderstood by some researchers, which is caused by the ambiguous study on primary migration. It is necessary to make a comparison of hydrocarbon expulsion between these two kinds of organic-rich sediments.

The Upper Triassic Yanchang Formation is one of the dominated exploration targets in Mesozoic petroleum system of Ordos Basin. Yanchang Formation, a whole depositional cycle of a lacustrine basin, can be divided by lithology into ten members (Chang 1 to Chang 10) from top to bottom (Zhao et al., 2006). When Chang7 Member was deposited, the lacustrine basin subsided and expanded rapidly due to Indosinian movement (Deng et al., 2008). Before the peak stage of hydrocarbon generation and expulsion, fine sediments had experienced continuous and strong compaction for a long time, which led to low porosities of current organic-rich deposits averaging 1%. The results calculated from simulations revealed that the excess pressures of Chang7 shale were merely 2-3MPa, because of the small successive thickness and twice tectonic uplifts in late Jurassic and Triassic. Besides, the montmorillonites have been dehydrated and converted to illite-montmorillonite mixed-layer before the main stage of hydrocarbon generation and expulsion. In consequence, the compaction and the dehydration of clay minerals have a limited impact on hydrocarbon primary migration. Expansive forces caused by hydrocarbon generation may play a great role in hydrocarbon expulsion of Triassic Chang7 source rocks (Zhang et al., 2006b). Moreover, Chang6 and Chang8 reservoirs adjoining to the Chang7 organic-rich sediments are featured by low permeability and porosity, which may also influence petroleum primary migration. Thus, Chang7 organic-rich deposits would display distinctive attributes on hydrocarbon expulsion which need further investigations and researches.

2. Geologic and geochemical characteristics
The Upper Triassic Yanchang Formation well-known for low porosity and low permeability reservoirs is one of the dominated exploration targets in Mesozoic petroleum system of Ordos Basin. Yanchang Formation, a whole depositional cycle of a lacustrine basin, can be divided by lithology into ten members (Chang 1 to Chang 10) from top to bottom (Zhao et al., 2006). When Chang7 Member was deposited, the lacustrine basin subsided and expanded rapidly due to Indosinian movement (Deng et al., 2008), consequently a large scale of organic-rich sediments were deposited in deep to semi-deep water of the lake (Zhang et al., 2006a). This series of organic-rich source rocks with a relatively stable thickness is critical in hydrocarbon accumulation in low-permeability and tight oil reservoirs, and is also the object of shale oil. The source rocks could be classified into two categories, oil shale and dark
mudstones. Vertically, the oil shale is mostly ranges in thickness from 10-40m at the bottom of Chang 7 Member, while the thickness of mudstones can be up to 110m mainly at the middle and top of this member. Their horizontal distributions are complementary; the oil shale is mostly distributed in deep lacustrine with a max thickness in Huanxian-Zhengning regions, whereas the mudstones are largely distributed in semi-deep lacustrine with larger thickness in the north-western and south-eastern areas.

Chang7 shale and dark mudstones vary in petrology, mineralogy and geochemistry. First of all, the shale is abundant in identified beddings and organic laminae, while the mudstones have few beddings and the organic matters are distributed dispersedly. Furthermore, they have many differences in mineral compositions, Chang7 shale are more rich in pyrites but less abundant in clay minerals, whereas the dark mudstones have more contents of clay minerals with less abundance of pyrites. More importantly, these two kinds of source rocks are various in organic geochemistry, which has an implication for hydrocarbon generation and expulsion. The shale has extremely high compositions of organic matters with the total organic carbon contents (TOC) mainly ranging from 6% to 20% averaging 14%, and the maximum TOC value is up to 30%. By comparison, the mudstones are also rich in organic matters, but the mean proportion is about 4%, which is much lower than that of the shale. Analysis on organic macerals reveals that kerogens of both the shale and the mudstones abound with liptinite whose content is mostly over 90%. While they have few abundance of exinite, and the other two types of constituents are quite low. In addition, the percentages of the liptinite macerals for shale is slightly higher than those for mudstones. As the burial depth of the shale and the mudstones is similar with the same thermal history and geological process, the mature degree is approximately alike at the peak stage of oil generation. The characteristics of hydrocarbon generation and expulsion from oil shale and mudstones can be distinguished by comparative studies on geochemical data.

3. Geochemical evidences for hydrocarbon expulsion

3.1. Lower Conversion Rates of Residual Bitumen "A" for Shale

Geochemistry study has displayed that the organic matters of shale and mudstones are similar, which are dominated by exinite belonging to the sapropelic groups. As a result, the hydrocarbon generation ratios are supposed to be almost the same at one level of maturity. In order to observe the process of hydrocarbon generation, one shale sample of low maturity was selected to carry out a thermal simulation experiment (Yang and Zhang, 2005; Zhang et al., 2006b). It was indicated that the cumulated oil productivity of the source rock was about 400kg/t, similar to that of the Eogene source rocks of Huanghua Depression in Bobaibay Basin of China. However, the conversion rate of residual bitumen "A" is very low especially for the samples with TOC higher than 10% (Fig.1). For the samples with TOC lower than 10%, the ratios of bitumen "A" and TOC are reducing with TOC going up. While the conversion rates of residual bitumen "A" stay at 5% for the samples with TOC higher than 10%, which may indicate that the controlling factors for hydrocarbon expulsion become simple when the source rocks are enriched with exceedingly high contents of organic matters. But for the samples with low organic matter abundance, the influences of petroleum primary migration would be more complicated, such as the deposits heterogeneity, fracture development, rock porosity etc. High cumulated oil productivity up to 400kg/t (40%) contrast to low conversion rate of residual bitumen "A" as low as 5% demonstrates that a lot of hydrocarbons have been expelled out of the organic-rich source rocks. In general, much more hydrocarbons of the shale samples have been expelled than those of the mudstones.

3.2. Lower Productivity Indexes and Lower Hydrogen Indexes for Shale

Similar to the conversion rates of residual bitumen "A", the productivity indexes (Ip=S1/S1+S2) and hydrogen indexes (HI=S2/TOC) of the tested rock samples are reducing as the organic matter enrichment is elevating (Fig.2, Fig.3). The S1 and S1+S2 ratios drop down to 0.1–0.2 when the TOC contents are more than 10% (Fig.2). Additionally, the majority of shale samples have relatively low indexes of hydrogen (HI) less than 400 milligrams per gram (Fig.3), which was supposed to be much higher because of the dominated compositions of the sapropelic groups in kerogen and the mature
stage at oil generation summit. It is predicated that both low values of $S_1/(S_1+S_2)$ and low ratios of $S_2/TOC$ for organic-rich source rocks are caused by intense hydrocarbon expulsion. Clearly, it can be concluded that the shale samples expulse pretty more hydrocarbons than the dark mudstones. Therefore, the researchers should note that the results on organic matter identification and source rock evaluation would be missed based on thermal pyrolysis. As indicated by the thermal pyrolysis data, the organic matter types of most source rocks are classified into type II which is not consistent with the consequence of detection under microscope. The source rock potential would be underestimated if the hydrocarbon expulsion degree hasn’t been considered.

3.3. Lower Ratios of Saturates/aromatics but Higher Contents of Polar Components of Residual Bitumen "A" for Shale

When the hydrocarbon of source rocks were highly expulsed, the geologic chromatographic effect of primary migration would be quite obvious. By comparison with the crude oils, the hydrocarbon group analysis of the residual bitumen "A" shows that the saturated hydrocarbons and the aromatics compositions of the shale and dark mudstones are lower than those of the crude oils. Particularly for the shale samples with abundant organic materials, the saturated group concentration is dramatically low with a range of 20%~55%. Besides, the ratios of saturates and aromatics for the shale samples are really lower than those of the mud rocks and accumulated oils. While the polar components contents including nonhydrocarbons and asphaltene of the shale are extremely higher than those of the mudstones and oils. And compared with the crude oil, dark mudstones only have a little higher abundance of polar components. The positive relationship between organic matter enrichment and polar components contents (Fig.4) manifests that the geochromatography effect gets more evident with TOC contents increasing. So, it can be speculated that the source rock quality is more superior, the degree of hydrocarbon expulsion would be enhanced.

3.4. Heavier Stable Carbon Isotopes of Residual Hydrocarbons for Shale

Except for the above-mentioned effect of geologic chromatographic, another influence, isotopic fractionation effect, caused by strong hydrocarbon expulsion of source rocks can also be apparent. Due to similar kerogen types and mature degree, the shale and dark mudstones ought to have bare difference on stable carbon isotopes, however, the outcome is not. The stable carbon isotopes of individual hydrocarbons of the shale samples are commonly heavier than those of the dark mudstones (Fig.5), which may have relationship with greater degree of petroleum expulsion. So, it is necessary for researchers to notice this result when the oil-source correlation is investigated, otherwise, the study would be misdirected.

3.5. Much Higher Hydrocarbon Expulsion Efficiency for Shale

Hydrocarbon expulsion efficiency refers to the percentage of expelling hydrocarbons from the total generating hydrocarbons. And the quantity of expelling hydrocarbons is the difference between the total hydrocarbon generation and the residual hydrocarbons. The oil productivity rates and conversion rates are necessary for calculation of hydrocarbon expulsion efficiency. The oil productivity rate of Chang7 shale and mudstones may be assigned as 400kg/t according to the properties of organic matter
and the thermal simulation experiment. As the light hydrocarbons (less than C_{14}) were missing, the conversion rate of residual bitumen "A" should be recovered using light hydrocarbon compensation coefficient (1.43). Source rock samples with the same kerogen type I and Ro of 0.90%-1.15% were collected to calculate the hydrocarbon efficiency. It is pointed out that the hydrocarbon expulsion rates of the shale samples are mostly ranging from 55% to 90% averaging 70%, while those of the dark mudstones are much lower with an average of 40% (Fig. 6). This calculation proves again that the shale has expelled much more hydrocarbons than the dark mudstones, which is accordant with the above evidences.

Fig. 4 Cross plot of TOC and polar components for shale and dark mudstone.  
Fig. 5 Stable carbon isotopes for residual normal alkanes of shale and dark mudstones.  
Fig. 6 Calculated hydrocarbon efficiency of shale and mudstone samples.

4. Significance on Mesozoic petroleum system
4.1. Importance for Low Permeability and Tight Oil Reservoirs
Firstly, this study is significant on source rock evaluation and oil-source correlation; high rates of hydrocarbon expulsion may bring about abnormal geochemical data which were commonly used in petroleum geology. If this phenomenon were neglected, the results might be unreasonable.

What’s more, Chang7 shale with exceptionally high degree of petroleum generation and expulsion play a key role in low-permeability and tight oil reservoirs in Mesozoic petroleum system. As the reservoir is so tight that the requirements for source rocks are pretty strict. Excellent source rocks are necessary for oil migration and accumulation in these kinds of reservoirs. The shale deposits not only provide main oil source rich in hydrocarbons but also the dominated driving force for petroleum migration through the tight conduits. Nevertheless, the dark mudstones are also important in some areas of Ordos Basin, for example the north western part of the basin.

4.2. Implications for the Future Evaluation on Shale Oil
It should be noted that although the hydrocarbon expulsion of Chang 7 shale is intense, the concentrations of the residual hydrocarbon in situ which is also called shale oil are still very high with an average of bitumen "A" at 0.80%. The residual bitumen “A” content is slightly lower at a mean value of 0.65%. Accordingly, shale oil (gas) stored in Chang7 organic-rich sediments would become an important fungible field for rising reserves in future.

Studies on the properties of the residual hydrocarbons have been revealed that the shale samples have a quite high content of polar components especially the asphaltene which is far more than those of the dark mudstones. It seems that the shale oil properties in Chang7 Member are not so well that they do not deserve investment and exploitation. However, we should take it into account that high contents of polar components are related to chromatographic effect caused by primary migration. More importantly, the asphaltene contents are positively associated with the organic matter abundances implying that the asphaltene is mainly absorbed by kerogen during the initial process of hydrocarbon expulsion. Therefore, abundant asphaltene in the residual bitumen "A" might not affect the fluidity of shale oil, which needs further studies in the future.

5. Conclusions
(1) Chang7 shale and dark mudstones have many differences on petrology, mineralogy and geochemistry. Therefore, they are distinguished on hydrocarbon expulsion.

(2) The shale sediments have extremely high efficiency of hydrocarbon expulsion with an average value of 70%, which resulted in several geochemical evidences and some unusual data. We should pay attention to this when source rock is evaluated and the oil-source correlation is carried out.

(3) The shale deposits with high rates of oil expulsion are not only critical for low-permeability and tight oil reservoirs, but also significant on future shale oil exploration.

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