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Discussion about the contribution of water to the shale gas reserves within high-over matured shale rocks

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Abstract. The shale gas currently exploited in China is mainly featured by high thermal maturity level and the methane concentration is generally more than 95% (v/v). The H/C atomic ratios of residual kerogen gradually decreased with the maturity whereas the source of elemental hydrogen contribution to the shale gas generation within high-over matured shale rocks is still vague. In recent years, some work indicated that the methane generation and its hydrogen isotope characteristics were greatly affected by elemental hydrogen from external water at the over-mature stage in shale rocks. The significance of water should be probed in the processes of geochemical degradation of residual kerogen and hydrocarbon generation in shales. It will be very meaningful to perform the hydrous pyrolysis experiments with heavy water to quantitatively appraise the impact of water on the hydrocarbon generation within shale rocks. A better understanding of the role that water plays on the shale gas generation and enrichment can be hopefully attained.

1. Introduction

The shale gas currently exploited in China is mainly featured by high thermal maturity level, buried in great depth and with a high dryness index concerning its hydrocarbon compositions (Fig. 1). Among the hydrocarbon molecules, the methane concentration is generally more than 95%, while the H/C atomic ratios of kerogen tend to decrease with maturity [1-2]. As the main component of shale gas, the H/C atomic ratio in methane is 4:1, which means that essentially methane generation is a process of massive hydrogenation and the hydrogen of it mainly comes from the dehydration condensation of another part of organic matter. However, with the development of study, it is confirmed by experiments and geological practice that the external hydrogen may play an important impact on the formation of natural gas during the hydrocarbon generation process. In recent years, more and more researches have shown that formation water and shale had undergone complex physical-chemical interactions in diagenesis [3-6]. Hence the significance of water should be probed in the processes of geochemical degradation of residual kerogen and hydrocarbon generation in shale. Otherwise, the associated role of water, residual kerogens, and clay minerals in the rocks are important to affect the production and composition of shale gas and other geochemical characteristics of shale reservoirs. Up to date, it is not clear with respect to the geochemical/physiochemical mechanisms of water and

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hydrocarbon-water-rock synergies in hydrocarbon generation processes that occurred inside shale rocks.

Figure 1. Schematic diagram showing the distribution of shale gas explored and exploited in China. [7]

2. Geochemical characteristics of shale gas

The humidity of high-over-mature shale gas is usually less than 5% [8]. For example, the composition of Longmaxi shale gas in Sichuan Basin is dominated by hydrocarbons, of which methane CH₄ accounts for 95.52-99.59% (mean CH₄ = 98.54%), while ethane (C₂H₆) (0.48%) and propane content are low as shown in Figure 2.Longmaxi shale gas is one kind of typical dry gas whose dryness coefficient (C1/C1-4, %) averages 99.5% [9-12]. Non-hydrocarbon gases include a minor amount of CO₂ (0.01%-1.48%) and N₂ (0%-2.95%).

It is greatly different between high-over-mature shale gas and low mature shale gas. Although the shale gas composition of Chang 7 member of the Yanchang Formation in Ordos Basin is dominated by hydrocarbons, the CH₄ content of Yanchang shale gas accounts for 76.09%-91.68% (mean CH₄=84.9%) obviously less than that of Longmaxi shale gas. Meanwhile, the content of ethane (6.83%) and propane (3.32%) is higher than that of Longmaxi shale gas [13]. Especially compared with the butane content (1.32%) in Yanchang shale gas, it is barely detected in Longmaxi shale gas (Fig. 2). Non-hydrocarbon gases of Yanchang shale gas include CO₂ and N₂ and their contents are less than 1.0%.



Figure 2. Relative proportions of hydrocarbon components of Longmaxi and Yanchang shale gas from Sichuan and Ordos Basin, respectively.

The kerogen in shale hardly undergoes thermal cracking at the immature-low maturity stage, yet it could still produce a small amount of methane [14]. At a higher mature stage, the dominant products from thermal cracking of residual kerogen are liquid hydrocarbons [14-15], followed by small hydrocarbon molecules and methane. For example, the TOC content and thermal maturity of the shale sample in the Chang 7 Formation (type I kerogen) are 6-14% and 0.7-1.2%Ro, respectively. And the sample has a high content of C2-C5 at the stage of a sharp rise in the oil generation [13]. At the highover maturity stage, the principal products from thermal cracking of kerogen are methane and small hydrocarbon molecules, and there is almost no liquid hydrocarbon in shale rock. However, the liquid hydrocarbon and small hydrocarbon molecules formed at the previous stage might be converted into shale gas at the high matured stage. Longmaxi shale gas is severely deficient in C2-C5 small molecular hydrocarbon. This implies that C2-C5 can be degraded to form methane meanwhile residual kerogen is degraded to generate small molecular hydrocarbons, which is instrumental in improving the drying coefficient of shale gas. Simulation experiments have shown that some minerals can catalyze the degradation of small molecular hydrocarbons in the presence of water [16-17], whose results are similar to high-over mature shale gas in the drying coefficient, the composition, and isotopic distribution characteristics, indicating that water may play an important role [18].



Figure 3. Hydrogen isotopic series of alkanes of Longmaxi shale gas and Yanchang shale gas.

The alkane hydrogen isotopic composition of Longmaxi shale gas in the Sichuan Basin illustrates that the hydrogen isotope values of methane and ethane are heavy. $\delta^2 H_{CH4}$ values of the Longmaxi shale gas range from -163‰ to -136‰ (mean $\delta^2 H_{CH4}$ =-148.3‰) and $\delta^2 H_{C2H6}$ values are in the range of -224‰ - -128‰ (mean $\delta^2 H_{C2H6}$ =-173‰). Hydrogen isotope values of methane of Yanchang shale gas are from -237‰ to -277‰, the average of which is -256‰. $\delta^2 H_{C2H6}$ values are in the range of -182‰--286‰ (mean $\delta^2 H_{C2H6}$ =-244‰) and $\delta^2 H_{C3H8}$ values range from -170‰ to -203‰ (mean $\delta^2 H_{C3H8}$ =-188‰) [13, 19]. Figure 3 notes that comparing with Yanchang shale gas, the $\delta^2 H_{CH4}$ and $\delta^2 H_{C2H6}$ values of Longmaxi shale gas are much heavier.



Figure 4. Relationship between Ro and hydrogen isotopic series of alkanes in Longmaxi shale gas and Yanchang shale gas.

The $\delta^2 H_{CH4}$ and Ro value of the sample in Longmaxi Formation implies a significant negative correlation whereas a negative correlation tendency exists between $\delta^2 H_{C2H6}$ and the Ro value even though it isn't very clear. $\delta^2 H_{CH4}$ and $\delta^2 H_{C2H6}$ values display no obvious correlation with Ro in Yanchang Formation (Fig. 4). It has now become evident that the hydrogen isotopic composition of Longmaxi shale gas is significantly heavier than that of Yanchang shale gas, indicating that the water in the depositional environment may have an extremely important influence on the alkane hydrogen isotopic composition of shale gas. In other words, if the elemental hydrogen from water can participate in the process of shale gas generation, the hydrogen isotopic composition of shale gas will be affected by the external water under high-over thermal maturity [3, 20]. Proved by hydrous pyrolysis simulated experiments, the hydrogen isotope of production is influenced. Yet the specific mechanism and molecular detail are poorly understood [18, 21]. Apart from this work, future research should be concerned on further geochemistry significance and practical geological application about water.

3. Future study

By comparing shale gas composition and alkane hydrogen isotopic data above, it must be pointed out that there is a huge difference between samples within high-over and low matured shale rocks. The methane generation and its hydrogen isotope characteristics are greatly affected by elemental hydrogen from external water at the over-mature stage in shale rocks. Otherwise, the source of elemental hydrogen contributing to the shale gas within high-over matured shale rocks is still vague. Researches illustrate that water molecules in the shale reservoirs may play an important role in the gas hydrocarbon generation at the high-over mature stage, which cannot be ignored. In addition, the hydrocarbon-water-rock interaction also has a huge impact whereas the mechanism of its synergy is still unclear. In summary, the comparison of data reveals the need for further experimental work should be carried out to investigate the geochemical-physiochemical mechanisms of water to the shale gases within high-over matured shale rocks.

We plan to launch a series of hydrous pyrolysis experiments with heavy water to quantitatively appraise the impact of water on hydrocarbon generation within shales. The extent and position of

deuterium substitution in a variety of hydrocarbon structural types is going to be measured by mass spectrometry. The isotopic transfer of water hydrogen to hydrocarbons generated can be quantified. Meanwhile, the physical and chemical properties of residual kerogen should be analyzed and compared before and after the reactions. We expect to learn how water participates in the reactions and gain some insight into the mechanisms controlling the contribution of water hydrogen to hydrocarbon gas generation in sedimentary basins. A better understanding of the role that water plays on evaluating the potential of shale gas generation and formation can be offered.

Acknowledgments

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