Carbon Isotope Reversals of Changning-Weiyuan Region Shale Gas, Sichuan Basin

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1 Introduction

Many high yield shale gas areas in the World are discovered carbon isotope reversals: Barnett, Fayetteville (Zumberge et al., 2012), Marcellus (Tilley et al., 2013), Haynesville (Ferworn et al., 2008), Albany shale gas (Gao et al., 2014), Utica shale gas (Xia et al., 1999; Xia et al., 2012; Xia et al., 2013), the Foothills (Tilley et al., 2011), Horn River (Tilley et al., 2013) and Ordos basin shale gas (Wang et al., 2015; Dai et al., 2005). The occurrence probability of carbon isotope reversals in shale gas is far higher than that of conventional gas plays. And, this isotopic abnormal phenomenon has become a typical characteristic of shale gas. Many data show that carbon isotope reversals can be used to indicate the overpressure in shale gas reservoir and shale gas higher yield (Zumberge et al., 2012; Gao et al., 2014; Tilley et al., 2013; Hao et al., 2013). However, isotope reversal occurred both at high and low production area in Marcellus (Madren, 2012). So, there are still different opinions about carbon isotope reversals indicating high yield of shale gas.

2 Carbon Isotopic Reversal Mechanism

Several reasons can result in carbon isotope reversals: (1) Hydrocarbon gas mixture of different origin: different maturity gas mixing, abiotic gas and biogenic gas mixing, such as the carbon isotope reversal of Ordovician and Silurian shale gas in Appalachian basin, New York. It caused by the deep and post-mature gas mixed (Jenden et al., 1993). (2) Secondary cracking of oil and hydrocarbon gas lead to carbon isotope reversals of C1 - C4 (Ni et al., 2011; Hao and Zou, 2013; Xia et al., 2013). In hydrocarbon cracking process, the larger the molecular weight of alkane the smaller activation energy they needed when cracking. Chemical bond of lighter isotopes ruptured easily, so low molecular weight of alkane components gradually enrichment of heavier isotopes (13C, D), in the process of evolution (Tang et al., 2005; Ni et al., 2011). (3) Segmented desorption experiments found that shale gas adsorption / desorption process caused the carbon isotopic fractionation (Wang et al., 2015). Carbon isotope fractionation will seriously affect the isotopic composition in the process of shale gas diffusion (adsorption / desorption). The clay minerals in low permeability shale will preferential adsorption 13CH4, which results in the enrichment of 12CH4 in the gas phase (Lu et al., 2015). Fractionation of carbon isotopes of methane in natural gas due to mass transport is evaluated based on statistical thermodynamics, microkinetics and fluid dynamics analysis (Xia et al., 2012). (4) After modified by water, organic material can react with water to cause abnormal distribution of the carbon isotope (Tang et al., 2011). Pyrolysis experiments of low-matured kerogen (type II) together with water show that water can promote the secondary cracking of C2+ components, the δ13C1 and δ2HCH4 values become more negative (Gao et al., 2014).

3 Carbon Isotopic Reversal in Changning-Weiyuan Region

The phenomenon of carbon isotope reversals are also found Changning-Weiyuan district in Sichuan Basin, China (Dai et al., 2014; Tang et al., 2013). Is there any relationship between carbon isotope reversal and high shale gas yield need further research. Therefore, we
studied the geochemical characteristics of residual shale gas and produced shale gas in Changning-Weiyuan dis region (Tang et al., 2015; Shang et al., 2014). And, three types of low mature organic-rich samples from US Green River shale (Type I kerogen), Woodford shale (Type II kerogen), and China Pearl River Mouth Basin (Type III kerogen) were chosen as the initial samples for pyrolysis simulation on hydrocarbon generation (Tang et al., 2013).

3.1 Produced gas carbon isotope

The results of carbon isotope analysis of produced shale gas in Changning-Weiyuan region show carbon isotopic reversals. Isotopically reversed trends (δ13C1>δ13C2) between ethane and methane were observed for all samples. And, δ13C1>δ13C2>δ13C3 is also found for some samples in Changing district. Post-mature source rock (Ro > 2.0%) generally experience kerogen cracking, oil producing, oil cracking and hydrocarbon gas cracking (Gai et al., 2015; Gao et al., 2014; Shang et al., 2013). In different stages, hydrocarbon cracking needs different activation energy, and it will produce cracking gas with different isotopic composition. In the closed system, Shale gas, produced by cracking of kerogen and liquid hydrocarbon in different evolution stages, have different carbon isotopic composition. Carbon isotopic reversals prone to occur in high matured shale gas (Dai et al., 2014).

3.2 Produce gas carbon isotope

The result of residual gas analysis showed that N2 and CO2 is the main composition (Tang et al., 2015). This indicates that gas released from the isolated pores in organic-rich shale preferentially retains N2 and CO2. After nor-malization to 100% total gaseous hydrocarbons, the crushed gas shows a CH4-dominated dry gas signature similar to the signature of produced gas. The carbon isotopic signatures of crushed gas show the reversal of carbon isotopic distribution patterns between methane and ethane. It demonstrated residual shale gas inheriting post-mature shale gas geochemical characteristics.

3.3 Pyrolysis simulation experiments of Low-mature Shale

Maturity and evolution of shale carbon play a critical role about carbon isotope reversal in closed system (Tilley et al., 2013). Pyrolysis simulation experiments were carried out with three different types of low-mature shale collected from Green River, Woodford and China Pearl River Mouth Basin. A pyrolysis system of sealed gold tubes in high pressure vessels was employed to conduct pyrolysis experiments. The results show that organic matter conversion from organic-rich shale to oil and gas can be divided into three stages: the stage of oil generation (Ro < 1.2%), oil cracking stage (< 1.2% Ro < 2.0%) and gaseous hydrocarbons cracking (Ro > 2.0%). In the oil cracking stage, a large number of secondary cracking gases will be produced with the increase of maturity. The content of secondary cracking gas can be up to 30% of the total volume. And methane and ethane carbon isotope will change (Xia et al., 2013). The average value of Ro is 2.69% for Longmaxi shale in Weiyuan - changning region (Chen et al., 2011). Organic matter is in the stage of gaseous hydrocarbon cracking. The production of shale gas is at the peak. Shale gas in this region have high methane content (NH2-2 Well: 98.59%) and high dry coefficient (> 99%). So, carbon isotope reversals possibly indicate high yield in post-mature shale gas play.

3 Conclusion

Produced shale gas carbon isotope is heavier than residual shale gas for CN07. Compared with lighter isotope molecules (12CH4), heavier isotopes molecules (13CH4) are preferential adsorbed and hysteretic desorbed, in shale gas diffusion process (Lu et al., 2015; Chen Run etc., 2007). In the core desorption experiments, δ13C1 become heavier with shale gas desorption degree increase (Wang et al., 2015). Methane carbon isotope of shale residual gas is heavier than production gas. It is indicating that heavier isotopes molecule (13CH4) is preferential adsorbed in shale. The capacity of adsorption is affected by migration distance and formation pressure. Mass Transportation affects the composition of methane carbon isotope.

From what has been discussed above, we can get the following conclusions: Shale in Cangning - Weiyuan region is high maturity. Gaseous hydrocarbons cracking lead to the abnormal distribution of carbon isotope composition characteristics. Carbon isotopic reversals are expected to indicate high yield of shale gas in this region. In closed system, the residual shale gas can inherit gas geochemical characteristics of designated mature stage of shale gas. Adsorption/desorption effect can cause carbon isotope fractionation. And isotope fractionation degree is related to the factors such as migration distance and formation pressure.

References


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