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The Origin and Significance of Abnormally Heavy Ethane Carbon Isotope of Natural Gas - Based on the case of Qishen-1 well

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Deep formations of Shasan Member (Es_3) of Qikou Depression have rich hydrocarbon resources. Being an important exploration domain of Dagang Exploration Area, this area has been explored with low degree and low proved rate, and no profound breakthrough has been made. The investigation on Deep formations of Qikou Depression was conducted with the support of the CNPC, and Qishen-1 Well of risk exploration well was developed in fault nose of deep formation-1 of North Dagang structural belt. This well was completed with the well depth of 5,088m at Es3. During the process of drilling, several segments with excellent hydrocarbon show were encountered, and the following three sections showed an active gas. The gas reservoir by log interpretation was up to 189 meters / 49 floors. By DST (Drill Stem Testing), the daily output of 54611 square nature gas was obtained.

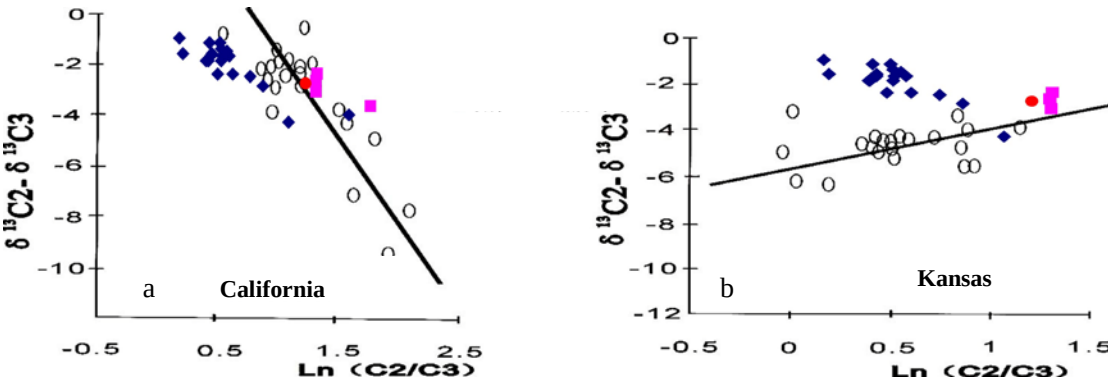
The well section of 4823.0 ~ 5088.0m are used for the sampling of natural gas in Qishen-1 well. Sample containers involve the gas bag, glass bottles and cylinders. The analysis and testing of the gas composition, carbon isotope and light hydrocarbon were conducted. The HP6890N chromatography was adopted for Gas composition analysis; the Finnigan Mat Delta Plus GC / C / IRMS system was used for carbon isotope analysis of natural gas; HP6890A gas chromatograph was used for light hydrocarbon analysis. Carbon isotope data were measured with the unit of parts per thousand relative to the PDB standard with the analysis accuracy of ± 0.1 ‰.

The natural gas of Qishen-1 well are mainly composed of hydrocarbon gases, with the methane content of 89.99% ~ 95.83%, which is the highest among depression regions. The Ethane content (C_2H_6) is between 4.3% ~ 6.35% with dry coefficient of 90.42% - 93.86%, showing the gas is rather moist. The sequence of $\delta^{13}C_1<\delta^{13}C_2<\delta^{13}C_3$ is shown in carbon isotope components. It can be seen that values increase with the increase of carbon number. $\delta^{13}C_1$ values of natural gas in Qishen-1 well are mainly distributed in the range of -32.7 ‰ - -35.7 ‰, which are heavier than those in other depression regions. $\delta^{13}C_2$ values are mainly distributed between -15.2 ‰ and -19 ‰, which are excessively heavier those of other depression regions and are also the heaviest $\delta^{13}C_2$ found in China. Dai Jinxing, an academician of Academy of Sciences, concluded that $\delta^{13}C_2$ of natural gas was mainly distributed between -22 ‰ and -37 ‰. While △

$^{13}C_{2\ -1}$ big difference (to 14.2 ‰ ~ 17.3 ‰), $\delta^{13}C_3$ mainly distributed in between -14.3 ‰ ~ -15.9 ‰. Benzene in C_6 series of light hydrocarbons of natural gas has a relatively high content of between 38% and 50%, while C_7 series compose of a relatively high toluene content of 35.7% ~ 55.2% and a low methyl cyclohexane content of 18.6% ~ 31.9%.

Previous studies suggest that ethane and other heavy hydrocarbon gas has a strong stable carbon isotope and inheritance of parent material type, and genetic analysis is conducted using carbon isotope of heavy hydrocarbon gas. The judgment standard of $\delta^{13}C_2$> -25.1 ‰ is proposed and $\delta^{13}C_3$> -23.2 ‰ stands that the natural gas is coal-formed gas. That is to say, the natural gas of Qishen-1 well would coal-formed gas relying solely on the determination of carbon isotopic in heavy hydrocarbon gases such as ethane. Nevertheless, methyl cyclohexane has a relatively low content in C_7 series, which is obviously contrary to the conclusions of coal-formed gas. Huang Difan (1996) suggests that methane is the main hydrocarbon in natural gas. Therefore, the results of gas genetic classification and mixed-sources of natural gas are not highly reliable when merely carbon isotopic in heavy hydrocarbon gases are taken into account, while it is more reasonable and effective using the method of combining isotopes, light hydrocarbons as well as components of natural gas. Recent studies suggest that carbon isotope of ethane and other heavy hydrocarbons may become very heavy with a high degree of thermal evolution and the role of parent material type is secondary. Natural gas of Qishen-1 well gas has a high abundance ratio of benzene and toluene, proving that the natural gas has experienced a high degree of thermal evolution.

The identification of carbon isotope and component characteristics of natural gas according to the classical chart (see Figure 1)of kerogen pyrolysis gas and crude oil pyrolysis gas shows that the natural gas of Qishen-1 well are between kerogen pyrolysis gas and crude oil pyrolysis gas. The test of hydrocarbon production simulation is conducted on duck grey mudstone of Es_3 of Qishen-1 well in closed system at different temperatures. Results show a good compatibility between natural gas and light hydrocarbons of thermolytical gas of dark mudstone at 500-700 ℃, both of which have a high abundance of benzene and toluene and a low abundance of n-heptane and methylcyclohexane, revealing natural gas of Qishen-1 well has a close relationship with the high-maturity stage of Es_3. Cramer, Shuai Yanhua et al. believe that carbon isotope of ethane can become very heavy through secondary cracking at high temperature, with the maximum of abundance up to -13 ‰ ~ -15 ‰. Through the analyzing on characteristics of gas composition, isotopes and light hydrocarbon, as well as thermal simulation on hydrocarbon source rock, it is believed that the abnormal heavy carbon isotope of ethane in natural gas of Qishen-1 well has a close relationship with hydrocarbon source rock of Es_3 and secondary cracking gas of oil at high-maturity stage.



a. kerogen pyrolysis gas b. crude oil pyrolysis gas

◆natural gas of Dagang oilfield ■Qishen-1 well gas ●5088m cylinder gas of Qishen-1

Figure 1 Identification chart of kerogen pyrolysis gas and crude oil pyrolysis gas

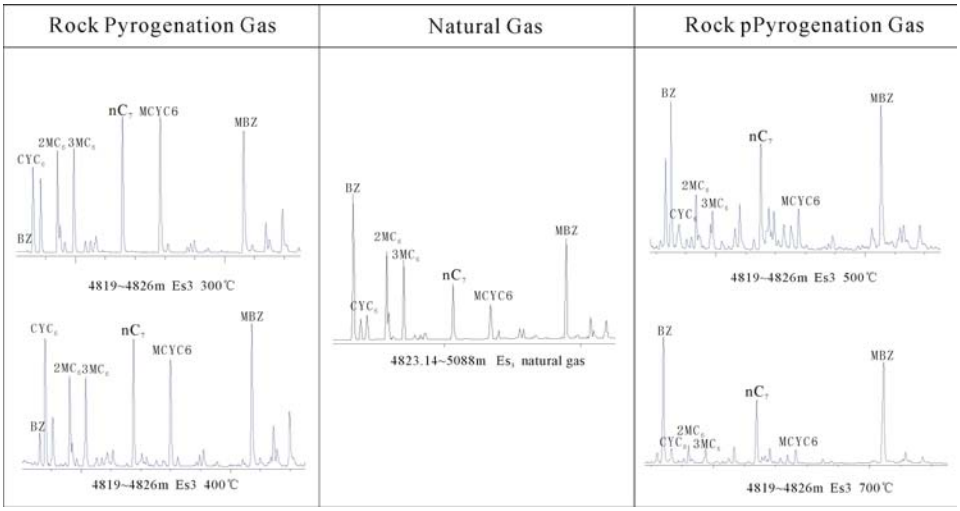


Figure 2 Comparison between natural gas of Qishen-1 well and light hydrocarbon of rock pyrogenation