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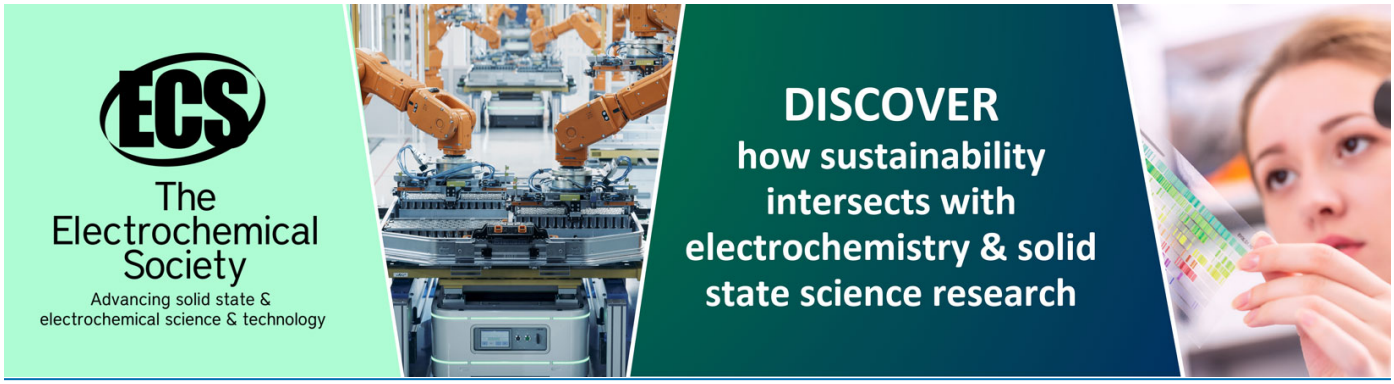

Identification to oil cracking in east of Sichuan Basin

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Abstract. In Sichuan basin the Lower Palaeozoic source rock has reached high to over-mature stage, but it is still considered that it has obvious genetic link with some gas reservoirs which were formed later. Therefore, the accumulation process between ancient high to over-mature source rock and the late formation of gas reservoirs has become one of the key factors to recognize the law of natural gas accumulation in Sichuan Basin. Based on some characteristics of Carboniferous gas reservoir in eastern basin, such as the gas compositions, stable carbon isotope, it is found that the gas reservoir is oil-cracking gas. The result reveals that the formation and evolution of present gas reservoir is that an ancient oil pool experienced the processes of forming, accumulating, destructing, and thermal maturating and cracking into gas reservoir.

1. Introduction

Similar to the process of kerogen that pyrolysed hydrocarbon, the thermally altered action (cracking) of crude oil in the oil reservoir is essentially a pyrolysis reaction at certain temperature, with the generation of gaseous hydrocarbon and residues (solid asphalt). Therefore, the course of reaction is consistent with the law of the chemical kinetics. It means that the cracking process of crude oil can be described by the equations of chemical kinetic. In recent years many scholars at home and abroad [1-11] have carried out the study of the reaction of pyrolysis crude oil using chemical kinetics and hermal history to quantitatively evaluate the degree of cracking of crude oil.

In the eastern Sichuan Basin the Lower Paleozoic Silurian source rock has reached high to over-mature stage. And vitrinite reflectance (Ro) reached more than 2% at present, with the distribution of 3.0 ~ 3.5% for majority of them, which illustrates that the hydrocarbon potential has been exhausted. However, a large number of gas reservoirs have been found in its overlying Carboniferous carbonate reservoir. Among the compositions in addition to the high concentration of methane (95.5 ~ 98%) in the gas reservoir, the surplus are in large quantities of solid carbon bitumen that remain in the carbonate reservoir [12].

The paper is based on the characteristics of chemical compositions and of stable carbon isotope of natural gas in Carboniferous gas pools in eastern Sichuan Basin, together with the study of the types of inclusions, homogenization temperature, composition, phase and solid asphalt, etc., to look for the evidence of thermal cracking of crude oil. At the same time, the chemical kinetics of cracking gas of

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crude oil is used to calculate the efficiency of the pyrolysis of paleo-oil pools. All the above are necessary to reconstruct the process that the paleo-oil reservoir cracked into gas reservoir.

2. Geological background

East Sichuan area is a relatively tectonically active zone in stable Sichuan Basin Block. It is adjacent to Huaying Mountains - Shilong canyon from west, east to Qiyue Mountains, north from Daba Mountains, south to Nanchuan-Kailong line, with an area of about $5.5 \times 10^4 km^2$. And it is a parallel fold area, which is in control of the great fault, with the predominance of high anticline zone. There are 10 rows of high steep tectonic belts primarily extending toward the east north-east from west to east. The current structure is an ejective fold of north north-east and north-east; the anticline belts often have many high focuses which present slimly extending tens of hundreds of kilometers, many Triassic carbonate rocks exposed at the structure core, steep or vertical inverted formations are at the flank area. The Syncline is broad with red clastic Jurassic rocks; the physiognomy is gentle hilly area and the terrain does not fluctuate greatly. The width ratio of high steep anticline and syncline is 1: 3, which shows an association feature of ejective fold. And the main anticlines formed accompanied by the great faults (Figure 1).

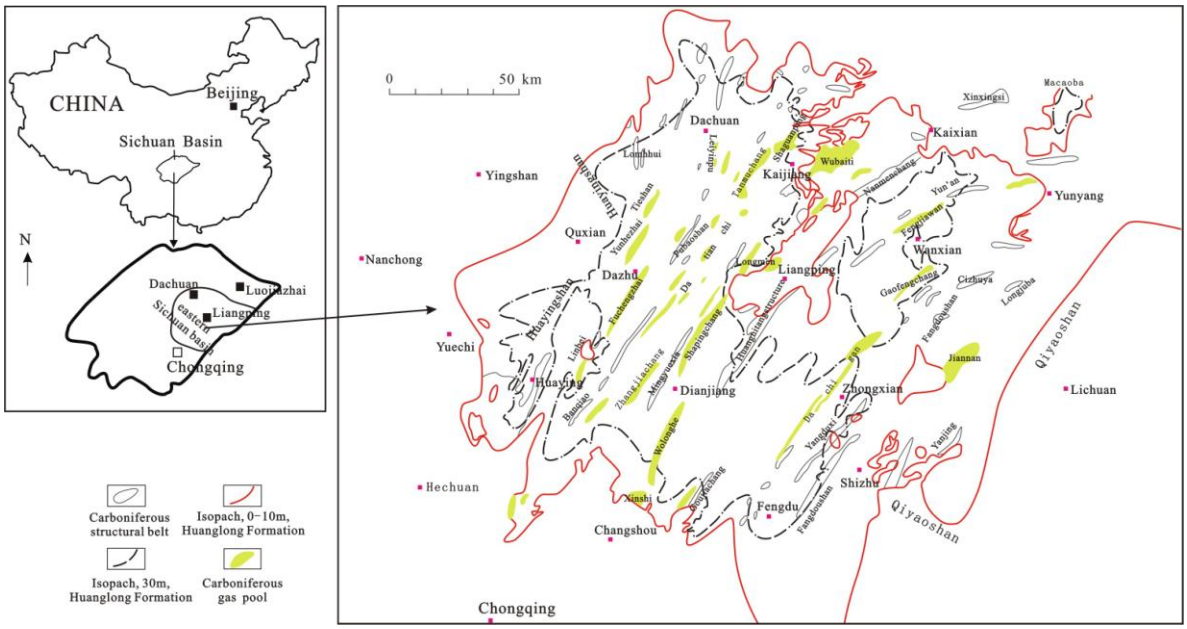

Figure 1. Distribution map of structure and large - medium size gas fields of east of Sichuan Basin.

In Sichuan Basin, as a major land-and-sea superimposed basin, there are multiple sets of source rock, multiple reservoir layers, changeable combination of reservoir and seal, multi-phase hydrocarbon generation, migration and accumulation process. In addition, Carboniferous gas reservoir is a relatively independent reservoir system which has its own source rock and reservoir layer. It is found that Chuandong Carboniferous gas reservoir sources is mainly from its underlying Silurian Longmaxi formation through comparison of gas source [13]; and the layer is the initial hydrocarbon source kitchen of Carboniferous reservoir.

Longmaxi formation is a black shale, dark gray mudstone and calcareous shale of deep water continental shelf facies, which is an anaerobic and reduction deposition. A few drillings reveal that the thickness of Longmaxi formation is about 300-672m in Chuandong area. The average thickness of graptolite shale facies of hydrocarbon source rock is about 400 m in the lower part, changing between 100-900m, and the thickness of high-quality hydrocarbon source rock of the black shale changes between 20-70m. More over, the content of organic carbon is high, with 0.5-7.5% in outcrop section. And the drillings reveal that the content of organic carbon is 0.07 ~ 2.77% (Well Wuke -1), which

indicates that it is a good set of source rocks that are the main gas source of the overlying Carboniferous gas.

3. Characteristics of gas composition

3.1. The chemical composition of gas

The hydrocarbon gas has an absolute advantage in gas components in Chuandong Carboniferous gas reservoir, with the content of the hydrocarbon gas 95.5 ~ 99.5%, mostly 97~98%. Methane is the main gas in total, even as high as 95.5 ~ 98% (figure 2a), which indicates that the gas is the typical dry gas, the drying coefficient 0.986 ~ 0.998. The content of heavy hydrocarbon gas is as low as 0.2-1.5%, generally including only ethane and propane, little butane. In addition, non-hydrocarbon gas accounts for only 1 ~ 4.5% (figure 2b).

3.2. Carbon isotope composition of gas

Methane carbon isotope values are between -37‰ ~ -29‰, at the top of -31‰ ~ -32‰ (figure 3), Ethane carbon isotope values are between -40 ~ -33%, Propane carbon isotope values between -39‰~ -32‰, $\delta^{13}C_1 > \delta^{13}C_2 < \delta^{13}C_3$; all of which suggest that carbon isotope value of ethane and methane reverses (Figure 4). Obviously, this shows that methane carbon isotope values increase with maturity. On the other hand, ethane carbon isotope values tend to increase along with methane carbon isotope values in Chuandong Carboniferous gas reservoir.

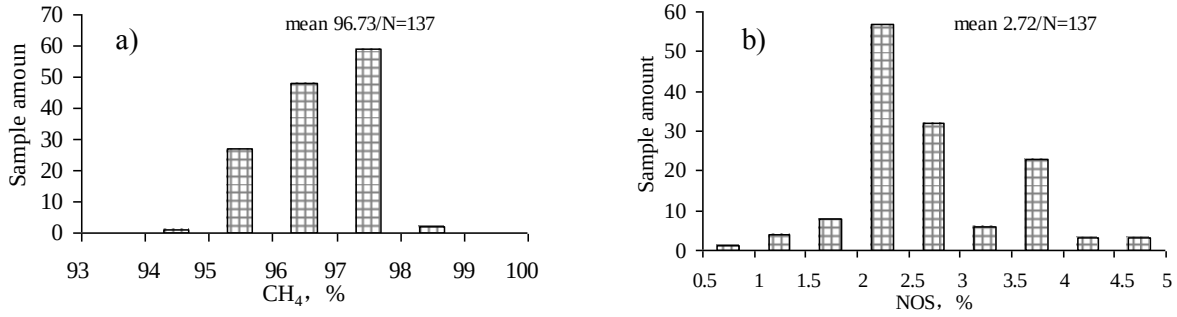

Figure 2. Frequency distribution of gas composition for the Carboniferous gas reservoir of east of Sichuan Basin.

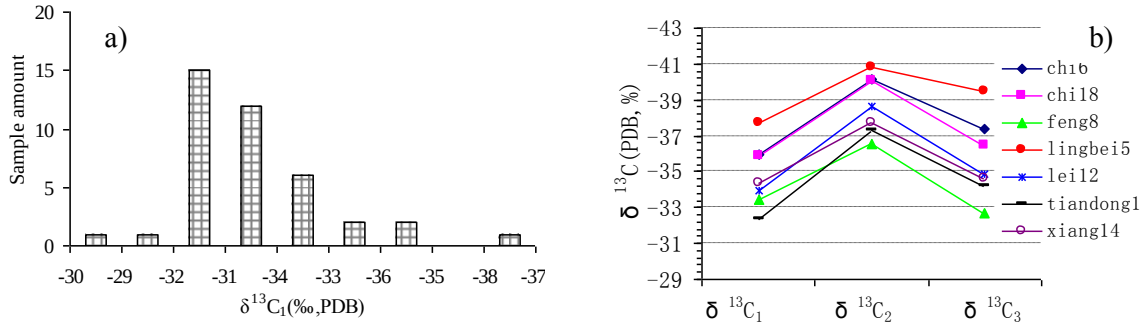

Figure 3. Distribution of Frequency and curve of carbon isotopes of Carboniferous natural gases.

4. According to gas composition to identify Crude oil cracking gas and kerogen pyrolysis gas

4.1. Identification mode of $ln(C_2/C_3)$ —$ln(C_1/C_2)$

Prinzhofer & Huc [14]. suggested to use the relevant charts of $\ln(C_2/C_3)-\ln(C_1/C_2)$ and $\delta^{13}C_2-\delta^{13}C_3$ and $\ln(C_2/C_3)$ to distinguish the Primary Cracking gas of kerogen and the secondary cracking gas of crude oil. But the two relevant diagrams are based on two principal aspects. Firstly, Behar et al. carried out thermal simulation experiments of the different types of kerogen (type II and type III) in a closed system [15]. The conclusion is the ratio of C_1/C_2 and C_2/C_3 of the kerogen Cracking gas (Primary Cracking) and the oil cracking gas(secondary cracking) are completely different, and the ratio of C_1/C_2 increases with Primary Cracking of kerogen, but remains stable with secondary cracking. On the contrary, the ratio of C_2/C_3 is basically the same during the Primary Cracking of kerogen, but increases rapidly during the secondary cracking. Secondly, the difference of $\delta^{13}C_2-\delta^{13}C_3$ of gas gradually decreases with maturity, which tends to zero.

Prinzhofer & Huc analyzed gas resources in Kansas and thought that the gases were from crude oil craking gas (Figure 4a) [14]. The relevant mode of $\ln(C_1/C_2)$ and $\ln(C_2/C_3)$ of gases is applied in Chuandong Carboniferous gas reservoir group. The ratio of $\ln(C_2/C_3)$ changes obviously in single gas reservoir; with vertical distribution, it changes more greatly in the entire Eastern Sichuan region. In single gas reservoir the data points of $\ln(C_1/C_2)$ nearly coincide, with small changes laterally and small changes totally. The result suggests that the gases are characterized by oil cracking gas (figure 4b).

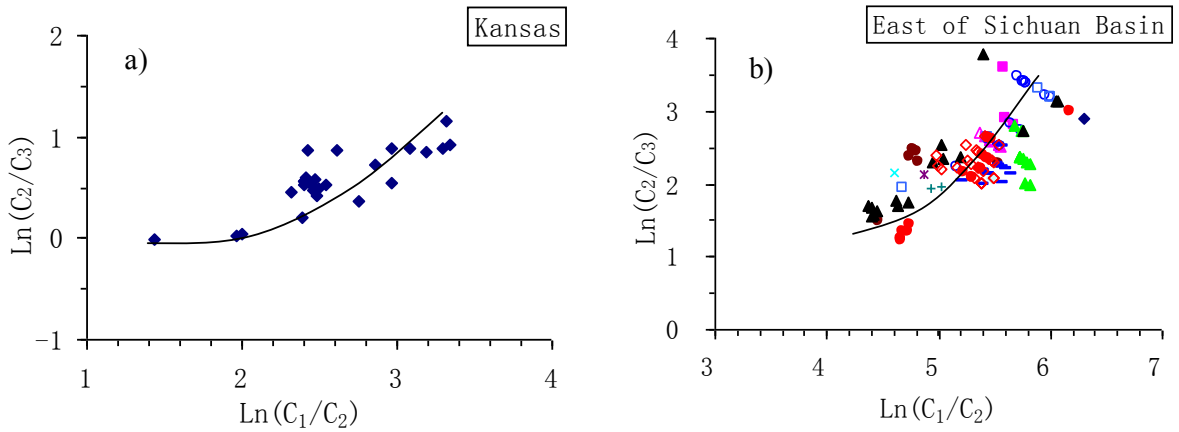

Figure 4. Correlation of C_1/C_2 and C_2/C_3 ratios for natural gases from from different area [16]

4.2. Identification mode of $\delta^{13}C_2-\delta^{13}C_3$ and $\ln(C_2/C_3)$

Prinzhofer & Huc established the diagram of $\delta^{13}C_2-\delta^{13}C_3$ vs. $\ln(C_2/C_3)$ in order to distinguish pyrolysis gases of kerogen and crude oil. The difference of$\delta^{13}C_2-\delta^{13}C_3$ of primary kerogen pyrolysis gas changes greatly totally, instead, $\mathrm{Ln}(C_2/C_3)$ basically does not change. The difference of $\delta^{13}C_2-\delta^{13}C_3$ of crude oil-cracking gas tends to be zero, whereas the value of $\mathrm{Ln}(C_2/C_3)$ increases. Prinzhofer & Huc applied the chart to conclude the gas source in Kansas was the crude oil-cracking gas (figure 5a). According to this chart, the gas source of Carboniferous gas reservoir is the cracking gas of crude oil in Eastern Sichuan region (figure 5b) with its $\delta^{13}C_2-\delta^{13}C_3$ tending to be zero.

5. Conclusion

In Lower Silurian Longmaxi Formation the high efficient hydrocarbon source rocks has come to high to over-mature (VRo as high as 2.5 ~ 3.5 %) in eastern Sichuan basin. This high efficient hydrocarbon source kitchen basically reached over the dead line of the oil generation between late Indosinian epoch and early Yanshannia epoch. The oil formed in Late Triassic - early Jurassic migrated upward and charged to the upper Middle Carboniferous carbonate reservoir to produce the Carboniferous ancient oil reservoir. Due to the increasing burial depth, the ancient oil reservoirs experienced crude oil cracking in the early Himalayan movement and turned into gas source kitchen. The gases generated

from the cracking of crude oil were stored in the existing Carboniferous reservoirs to form large Carboniferous gas reservoirs.

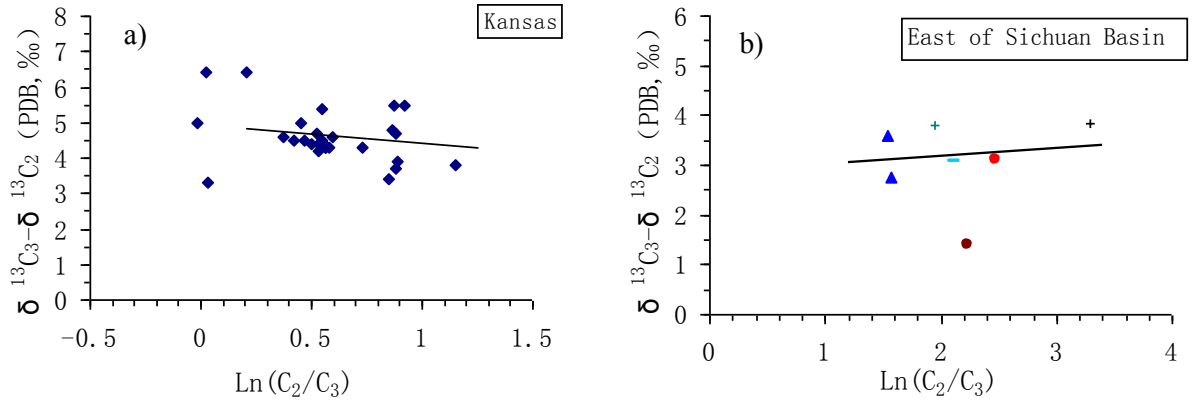

Figure 5. Plot of $\delta^{13}C_2-\delta^{13}C_3$ versus $\ln(C_2/C_3)$ for natural gases from different area.

Acknowledgments
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References

[1] Braun R L and Burnham A K. 1987 A nalysis of chemical reaction kinetics using a distribution of activation energies and simp lermodels Energy and Fuels **1** 153
[2] Burnham A.K., Gregg, H.R, Ward, R L, et al. 1997 Decomposition kinetics and mechanism of n-hexadecane-1,2-$^{13}C_2$ and dodece-1-ene-1,2-$^{13}C_2$ doped in petroleum and n-hexadecane Geochimica et Cosmochimica Acta **61** 3725-37
[3] Cramer B, Kross B M and Littke R 1998 Modelling isotope fractionation during primary cracking of natural gas: A reation kinetic approach Chemical Geology **149** 235-50
[4] Cramer B, Faber E, Gerling P, et al. 2001 Reaction kinetics of stable carbon isotopes in natural gas-insights from dry, open system pyrolysis experiments Energy & Fuels 15 517-32.
[5] Domine F. 1989. Kinetics of hexane pyrolysis at very high pressures. 1. Experimental study Energy and Fuels **3** 89-96
[6] Domine F 1991 High-pressure pyrolysis of n-hexane, 2,4-dimethylpentane and 1-phenylbutaneIs pressure an important geochemical parameter Organic Geochemistry **17** 619-34
[7] Horsfield B, Schenk H J, Mills N, et al. 1992 An investigation of the in-reservoir conversion of oil to gas, compositional and kinetic findings from closed-system pro-grammed-temperature pyrolysis Organic Geochemistry **19** 191-204
[8] Lu S F, Fu X T, Wang Z P, et al. 1996 The thermal kinetic models of kerogen to oil and kerogen to gas as well as its calibration Scientia Geologica Sinica **31** 15-21
[9] Quigley T M, Mackenzie A S, et al. 1988 The temperatures of oil and gas formation in the subsurface Nature **333** 549-52
[10] Ungerer P, Behar F, Villalba M, et al. 1988 Kinetic modelling of oil cracking.Organic Geochemistry **13** 857-68
[11] Waples D W 2000 The kinetics of in-reservoir oil destruction and gas formation: constraints from experimental and empirical data, and from thermodynamics Organic Geochemistry **31** 553-75
[12] Li Y X and Zhong N N 2007 Approach To Solid Migrabitumen Mechanism Of Carboniferous Gas Reservoir In The East Of Sichuan Basin Petroleum Geology & Experiment **29** 402-05

[13] Wang L S, Chen S J, Yang J J, et al. 2002 Geochemical mode of gas reservoir formation in carboniferous in east Sichuan Natur.Gas Industry supplementaty issue **22** 102-06
[14] Prinzhofer A A and Huc A Y 1995 Genetic and post-genetic molecular and isotopic fractionations in natural gases Chemical Geology **126** 281-90
[15] Behar F., Ungerer P., Kressmann S., et al. 1991 Thermal evolution of crude oils in sedimentary basins, experimental simulation in a confined system and kinetic modeling Revue de l'Institut Francais du Petrole **46** 151-83
[16] Jenden P D, Newell K. D, Kaplan I R, et al. 1988 Composition and stable isotope geochemistry of natural gases from Kansas, Midcontinent, U. S. A. In, M. Schell. Origins of Methane in the Earth Chem. Geol. **71** 117-47 (special issue)