## Research Advances

# The Openness Degree Study of the Jiaoshiba Shale Gas, Sichuan Basin, China-Potential Factor Responsible for Reversed Isotope Series 

ZHAO Heng ${ }^{1,2,3,4}$, LIU Wenhui ${ }^{5, *}$ and WANG Xiaofeng ${ }^{5}$<br>1 Key Laboratory of Mineral Resources in Coal Measures, China National Administration of Coal Geology, Key Laboratory of Shale Gas, China National Administration of Coal Geology, Jiangsu Geology and Mineral Resources Design and Research Institute, Xuzhou 221006,Jiangsu, China<br>2 Gansu Provincial Key Laboratory of Petroleum Resources, Key Laboratory of Petroleum Resources Research, Lanzhou Center for Oil and Gas Resources, Institute of Geology and Geophysics, Chinese Academy of Sciences, Lanzhou 730000, China<br>3 Wuxi Research Institute of Petroleum Geology, Sinopec Petroleum Exploration \& Production Research Institute, Wuxi 214151, Jiangsu, China<br>4 University of Chinese Academy of Sciences, Beijing 100049, China<br>5 Northwest University, Xian 710069, China

## Objective

Reversed alkane $\delta^{13} \mathrm{C}$ and $\delta^{2} \mathrm{H}$ values in many prolific shale plays all over the world have aroused much attention in the study of the formation mechanism of reversed isotope series in alkanes in the past few years(Zou Caineng et al., 2016). Although many researchers have put forward different hypotheses, the mechanism has not been well understood yet. The openness degree of oil and gas system has been neglected in previous studies which may be an important factor responsible for the isotope reversal. Since there is no isotope reversal in closed-system hydrocarbon generation simulation or open system hydrocarbon generation simulation, a relative open oil and gas system is necessary for isotope reversal. It is increasingly accepted that the mixing of natural gas from different maturity or source rock is a very important factor for reversed alkane isotope. However, the mixing effect of natural gas on isotope reversal is only effective on the premise that differential diffusion happens to different endmember in a relative open oil and gas system. Shale gas play is traditionally recognized as a closed selfsourced reservoir, however, more and more researches indicate that Jiaoshiba shale gas experienced multistage gas generation, migration and accumulation, similar with conventional natural gas reservoir. The objective of this study is to discuss the potential relationship between the openness degree of Jiaoshiba mudrock systems and the carbon isotopic reversal.

## Methods

A total of 29 wellhead shale gas samples were collected from the Jiaoshiba shale play. The alkane compositions of shale gas samples were analyzed using Agilent 6890N Gas chromatography. The carbon isotope of alkane in shale gas was measured using DELTA Plus XP mass spectrometer. The isotope analyses of He and Ar were carried out using quadrupole mass spectrometry (QMS). Since the concentration of He and Ar is very low in shale gas, the He and Ar elements were purified from shale gas in a noble gas purification system before isotope analysis. The shale gas was introduced into a $\mathrm{Zr}-\mathrm{Al}$ purifying furnace (held at $350^{\circ} \mathrm{C}$ for 20 min ) to remove $\mathrm{CO}_{2}$, hydrocarbons and other active gases. An aliquot of purified noble gases was then introduced to the gas getters for a second round purification, and then the noble gas was introduced into QMS for isotope analyses of He and Ar .

## Results

The Jiaoshiba shale gas in this study is dominated by methane, with an average concentration of $99.12 \%$. The carbon isotope of $\mathrm{C}_{1-3}$ in the Jiaoshiba shale gas are all in reversed isotope series $\left(\delta^{13} \mathrm{C}_{1}>\delta^{13} \mathrm{C}_{2}>\delta{ }^{13} \mathrm{C}_{3}\right)$. The $\delta^{13} \mathrm{C}_{1}$ values vary from $-32.7 \%$ to $-29.3 \%$ with an average value of $-30.7 \%$; the $\delta^{13} \mathrm{C}_{2}$ values vary from $-35.6 \%$ to $33.2 \%$ with an average value of $-34.8 \%$, and the $\delta^{13} \mathrm{C}_{3}$ values vary from $-37.7 \%$ to $-34.1 \%$ with an average value of $-36.2 \%$. The Jiaoshiba shale gas has ${ }^{3} \mathrm{He} /{ }^{4} \mathrm{He}$ values of 1.41 ppb to 1.69 ppb with an average value of 1.51 ppb , and $\mathrm{R} / \mathrm{Ra}$ ratios vary from 0.010 to 0.012 with

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Fig. 1. (a), Plots of $\mathrm{C}_{2} / \mathrm{C}_{3}$ versus $\left.\delta^{13} \mathrm{C}^{2} \mathrm{C}_{2}-\mathrm{C}_{3}\right]$ indicating that Jiaoshiba shale gases are derived from open system (modified from Xiao, 2011); (b), Plots of ${ }^{4} \mathrm{He}^{40} \mathrm{Ar}^{*}$ versus $\delta^{13} \mathrm{C}\left[\mathrm{C}_{2}-\mathrm{C}_{1}\right]$ indicating that Jiaoshiba shale gases are migratory natural gas (modified from Hunt et al., 2012).
an average value of 0.011 , indicative of a typical crustal origin. The ${ }^{40} \mathrm{Ar}{ }^{36} \mathrm{Ar}$ values vary from 9.96 to 19.8 with an average of 15.4 , far greater than the ${ }^{40} \mathrm{Ar} /^{36} \mathrm{Ar}$ value of air (295.5), indicating an overall stable conservation condition. The Jiaoshiba shale gas samples are distributed along the open system trend in Fig. 1a, suggesting that Jiaoshiba shale gas is derived from an open system. The enrichments of light noble gases ( ${ }^{4} \mathrm{He}$ and ${ }^{40} \mathrm{Ar}^{*}$ ), high production ratio of ${ }^{4} \mathrm{He} /{ }^{40} \mathrm{Ar}^{*}$ close to crustal production levels and reversed carbon isotope values between methane and ethane in Fig.1b indicate that the Jiaoshiba shale gas is a migratory natural gas $\left({ }^{40} \mathrm{Ar}^{*}\right.$ represents ${ }^{40} \mathrm{Ar}$ exclusively from radiogenic production).

## Conclusion

The openness study suggests that the Jiaoshiba shale gas is a migratory natural gas derived from an open system, which may be related with the multiple hydrocarbon accumulation process. Meanwhile, the far greater ${ }^{40} \mathrm{Ar} /{ }^{36} \mathrm{Ar}$ values of Jiaoshiba shale gas than that of air indicate an overall good conservation condition. Accordingly, the moderate openness degree of Jiaoshiba shale play is probably an important factor responsible for reversed isotope series. The detailed studies of differential accumulation and loss of hydrocarbons responsible for
isotope reversal during the multiple hydrocarbon generation and accumulation processes are in progress.

## Acknowledgments

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## References

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Zou Caineng, Yang Zhi, Pan Songqi, Chen Yanyan, Lin Senhu, Huang Jinliang, Wu Songtao, Dong Dazhong, Wang Shufang, Liang Feng, Sun Shasha, Huang Yong and Weng Dingwei, 2016. Shale gas formation and occurrence in China: an overview of the current status and future potential. Acta Geologica Sinica (English edition), 90(4): 1249-1283.
Appendix 1 Composition and isotopes of alkane and noble gas in the Jiaoshiba shale gas

| Well number | Alkane composition |  |  | Alkane isotope |  |  |  | Noble gas isotopes |  |  |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | $\mathrm{CH}_{4}$ | $\mathrm{C}_{2} \mathrm{H}_{6}$ | $\mathrm{C}_{3} \mathrm{H}_{8}$ | $\delta^{13} \mathrm{C}_{1}(\%)$ | $\delta^{13} \mathrm{C}_{2}\left(\%{ }_{0}\right)$ | $\delta^{13} \mathrm{C}_{3}\left(\%{ }_{0}\right)$ | $\delta^{13} \mathrm{C}_{2}-\delta^{13} \mathrm{C}_{1}$ | ${ }^{4} \mathrm{He}(\mathrm{ppm})$ | ${ }^{3} \mathrm{He} /{ }^{4} \mathrm{He}(\mathrm{ppb})$ | R/Ra | ${ }^{36} \mathrm{Ar}(\mathrm{ppm})$ | ${ }^{40} \mathrm{Ar}(\mathrm{ppm})$ | ${ }^{40} \mathrm{Ar}^{*}(\mathrm{ppm})$ | $\left.{ }^{40} \mathrm{Ar}\right)^{36} \mathrm{Ar}$ | ${ }^{4} \mathrm{He} /^{40} \mathrm{Ar}^{*}$ | ${ }^{38} \mathrm{Ar}{ }^{36} \mathrm{Ar}$ |
| JY0001 | 99.36\% | 0.62\% | 0.02\% | -29.7 | -33.7 | -34 | -4 | 311.3 | 1.43 | 0.010 | 0.023 | 32.63 | 25.85 | 1421.7 | 12.04 | 0.163 |
| JY0002 | 99.38\% | 0.60\% | 0.02\% | -30.5 | -35 | -36.4 | -4.5 | 315.4 | 1.41 | 0.010 | 0.022 | 32.63 | 26.12 | 1481.4 | 12.07 | 0.163 |
| JY0003 | 99.37\% | 0.61\% | 0.02\% | -31.2 | -34.7 | -36 | -3.5 | 338.5 | 1.53 | 0.011 | 0.018 | 30.06 | 24.61 | 1629.2 | 13.76 | 0.168 |
| JY0004 | 99.39\% | 0.59\% | 0.02\% | -30.6 | -35.6 | -36.3 | -5 | 335.4 | 1.55 | 0.011 | 0.023 | 33.18 | 26.44 | 1455.0 | 12.68 | 0.163 |
| JY0005 | 99.40\% | 0.58\% | 0.02\% | -30.8 | -34.9 | -37.7 | -4.1 | 297.6 | 1.52 | 0.011 | 0.019 | 29.79 | 24.16 | 1562.6 | 12.32 | 0.167 |
| JY0006 | 99.36\% | 0.62\% | 0.02\% | -30.1 | -33.2 | -35.2 | -3.1 | 281.9 | 1.69 | 0.012 | 0.032 | 32.09 | 22.57 | 996.1 | 12.49 | 0.169 |
| JY0007 | 99.38\% | 0.60\% | 0.02\% | -30.4 | -34.5 | -35.9 | -4.1 | 211.7 | 1.40 | 0.010 | 0.016 | 24.24 | 19.54 | 1525.4 | 10.83 | 0.167 |
| JY0008 | 99.40\% | 0.58\% | 0.02\% | -30.6 | -33.9 | -36.6 | -3.3 | 273.5 | 1.53 | 0.011 | 0.019 | 27.35 | 21.85 | 1468.7 | 12.52 | 0.172 |
| JY0009 | 99.40\% | 0.58\% | 0.02\% | -30.3 | -34.2 | -36.3 | -3.9 | 238.9 | 1.47 | 0.011 | 0.019 | 26.27 | 20.78 | 1412.9 | 11.50 | 0.161 |
| JY0010 | 99.40\% | 0.58\% | 0.02\% | -30.7 | -34.9 | -37.4 | -4.2 | 393.0 | 1.49 | 0.011 | 0.027 | 37.00 | 29.02 | 1369.4 | 13.54 | 0.183 |
| JY0011 | 99.37\% | 0.61\% | 0.02\% | -29.3 | -33.6 | -36.6 | -4.3 | 212.7 | 1.47 | 0.011 | 0.016 | 24.24 | 19.49 | 1508.8 | 10.91 | 0.167 |
| JY0012 | 99.37\% | 0.61\% | 0.02\% | -30.6 | -34.3 | -34.1 | -3.7 | 264.1 | 1.57 | 0.011 | 0.016 | 30.06 | 25.37 | 1894.3 | 10.41 | 0.163 |
| JY0013 | 99.42\% | 0.56\% | 0.02\% | -31.5 | -36.4 | -37.2 | -4.9 | 288.2 | 1.40 | 0.010 | 0.018 | 28.84 | 23.58 | 1620.4 | 12.22 | 0.160 |
| JY0014 | 99.36\% | 0.62\% | 0.02\% | -30.6 | -34.6 | -36.3 | -4 | 242.1 | 1.57 | 0.011 | 0.018 | 26.13 | 20.74 | 1430.5 | 11.67 | 0.161 |
| JY0015 | 99.47\% | 0.51\% | 0.02\% | -32.7 | -36.1 | -37.5 | -3.4 | 405.6 | 1.66 | 0.012 | 0.027 | 41.98 | 33.88 | 1532.3 | 11.97 | 0.161 |
| JY0016 | 99.36\% | 0.62\% | 0.02\% | -30.6 | -34.6 | -36.3 | -4 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| JY0017 | 99.41\% | 0.57\% | 0.02\% | -30.1 | -34.8 | -34.9 | -4.7 | 257.8 | 1.58 | 0.011 | 0.018 | 29.79 | 24.38 | 1627.2 | 10.57 | 0.159 |
| JY0018 | 99.36\% | 0.62\% | 0.02\% | -30.7 | -35 | -37.3 | -4.3 | 250.5 | 1.56 | 0.011 | 0.015 | 25.46 | 21.04 | 1701.6 | 11.91 | 0.170 |
| JY0019 | 99.30\% | 0.68\% | 0.02\% | -30.9 | -34.7 | -35.4 | -3.8 | 251.5 | 1.45 | 0.010 | 0.021 | 27.89 | 21.60 | 1309.2 | 11.65 | 0.163 |
| JY0020 | 99.62\% | 0.36\% | 0.02\% | -31.4 | -35.3 | -37 | -3.9 | 364.7 | 1.55 | 0.011 | 0.025 | 39.68 | 32.21 | 1571.4 | 11.32 | 0.164 |
| JY0021 | 99.57\% | 0.41\% | 0.02\% | -30.2 | -35.3 | -36.4 | -5.1 | 536.6 | 1.61 | 0.012 | 0.032 | 66.62 | 57.07 | 2061.7 | 9.40 | 0.169 |
| JY0022 | 99.54\% | 0.44\% | 0.02\% | -31.3 | -35.2 | -36 | -3.9 | 440.2 | 1.41 | 0.010 | 0.022 | 38.19 | 31.61 | 1716.2 | 13.92 | 0.160 |
| JY0023 | 99.35\% | 0.63\% | 0.02\% | -30.8 | -33.4 | -36.2 | -2.6 | 294.0 | 1.46 | 0.011 | 0.020 | 30.68 | 24.62 | 1496.9 | 11.94 | 0.164 |
| JY0024 | 99.33\% | 0.67\% | n.d. | -29.8 | -33.2 | n.d. | -3.4 | 298.0 | 1.44 | 0.010 | 0.023 | 29.96 | 23.30 | 1329.8 | 12.79 | 0.167 |
| JY0025 | 99.33\% | 0.67\% | n.d. | -30.3 | -34.3 | n.d. | -4 | 329.0 | 1.52 | 0.011 | 0.023 | 35.38 | 28.49 | 1516.4 | 11.55 | 0.165 |
| JY0026 | 99.34\% | 0.66\% | n.d. | -32.4 | -34.9 | n.d. | -2.5 | 329.0 | 1.55 | 0.011 | 0.025 | 32.25 | 24.87 | 1291.8 | 13.23 | 0.165 |
| JY0027 | 99.34\% | 0.66\% | n.d. | -29.8 | -33.5 | n.d. | -3.7 | 301.0 | 1.54 | 0.011 | 0.025 | 35.81 | 28.44 | 1434.7 | 10.59 | 0.170 |
| JY0028 | 99.36\% | 0.64\% | n.d. | -30.7 | -35.1 | n.d. | -4.4 | 322.0 | 1.49 | 0.011 | 0.020 | 40.09 | 34.12 | 1984.9 | 9.44 | 0.163 |
| JY0029 | 99.45\% | 0.55\% | n.d. | -31.0 | -35.5 | n.d. | -4.5 | 326.0 | 1.43 | 0.010 | 0.022 | 37.81 | 31.16 | 1680.7 | 10.46 | 0.164 |


[^0]:    * Corresponding author. E-mail: whliu@nwu.edu.cn

