Characteristics of desorption gas of lacustrine shale in the Ordos Basin, China

Jing Li¹,², Shixin Zhou¹,²*, Deliang Fu¹, Kefei Chen¹,², Chen Zhang¹,², Zexiang Sun¹,² and Pengpeng Li¹,²

¹ Northwest Institute of Eco-Environment and Resources, Chinese Academy of Sciences, Lanzhou 730000, China;  
² Key Laboratory of Petroleum Resources, Gansu Province, Lanzhou 730000, China  
³ Key Laboratory of Coal Exploration and Comprehensive Utilization, Ministry of Land and Resources, Shanxi Coal Geology Group Co., Ltd. Xi’an 710021, China

*Corresponding author’s e-mail: Sxzhou@lzb.ac.cn

Abstract. Desorption gases of four lacustrine shale cores from the Triassic Yanchang formation of the Ordos Basin, China were collected, and their molecular and carbon isotope compositions were analyzed in this study. Results show that hydrocarbon gases of desorption gas are dominated by methane with relatively low dryness coefficient ranging from 0.45 to 0.82. The δ¹³C values for hydrocarbon gases increase with increasing carbon number, and which for methane ranges from −57.15‰ to −53.71‰. The hydrocarbon gases generally derived from a mixed origin with primary contribution from thermogenic processes. Desorption gases of sample YK-340.7 could experience biodegradation for its relatively high dryness coefficient and (iC₄H₁₀ + iC₅H₁₂) / (nC₄H₁₀ + nC₅H₁₂) value. A significant depletion of ¹³C for methane was observed during desorption process, the reason for which could be differences in molecular mobility of the ¹²CH₄ and ¹³CH₄. Changes in the δ¹³Cethane and δ¹³Cpropane during desorption process are week.

1. Introduction
Shale gas is an important unconventional hydrocarbon resource and attracted remarkable attention in recent years. Natural gas in shale mainly stored as absorbed gas on surface of organic matter and inorganic minerals, as free gas within fractures and intergranular porosity, and as dissolved gas in kerogen, oil and water [1-2]. The adsorption state of the gas plays a critical role in the success of shale as a gas reservoir [3]. Shale gas systems are of two distinct types: biogenic and thermogenic, although there can also be mixtures of the two gas types [2]. Distinguishing between biogenic and thermogenic methane is essential for natural gas exploration and production strategies and improved resource estimates [4] and mainly relay on the geochemical study of chemical composition and carbon isotopic composition of hydrocarbons [5].

The desorption process of gas in shale is a combination of gas diffusion and desorption, both of which may result in isotope fractionation [6]. Zhang and Krooss [7] reported a significant depletion of ¹³C of methane in a simulated gas diffusion experiment of shale and pointed out that the depletion is higher in the initial non-steady state than in the steady state of the diffusion process. Xia and Tang [6] evaluated the fractionation of carbon isotope of methane during natural gas flow with coupled diffusion and adsorption/desorption through a continuum flow model and indicated that isotopic
fractionation was mostly dominated by mass transport, rather than the fractionation between adsorbate phase and gas phase. They also pointed out that degassing processes under geological processes were unlikely to bring about isotope fractionation larger than 5‰. But the carbon isotopic composition and chemical composition variation for hydrocarbons in gas desorption process of shale core has been poorly reported at present.

In this study, lacustrine shale cores from the Triassic Yanchang formation of the Ordos Basin, China were utilized. The desorption experiments were performed at the drill site immediately after the shale core samples were collected. The chemical composition and carbon isotopic composition for the desorption gases were analyzed, the genetic origin for the hydrocarbons and gas characteristics variation in desorption process were studied.

2. Samples and methods

Four shale cores from the Triassic Yanchang formation were utilized in this study. The core samples were collected from YK-1 well located in the south of the Ordos Basin, China. Detailed location and lithology information of YK-1 well has been reported in literature [8]. Sampling depth of the four core samples are 230.1m, 234.8m, 237.3m and 340.7m respectively. Each core sample was immediately placed into a metal sealed canister at the drilling site after collected. The desorbed gas was collected in a graduated glass bottle by discharging saturated salt brine. The glass bottle was replaced every 24 hours until the desorption rate is less than 10ml/24h. Then the desorption was performed at 40°C, 60°C, 80°C subsequently. The desorbed gas at each temperature was collected until the desorption rate is less than 10ml/24h.

The chemical compositions of the gas samples were determined by Agilent 6890N gas chromatograph (GC) equipped with a flame ionization detector and a thermal conductivity detector. Individual hydrocarbon gas components from methane to pentane (C$_1$-C$_5$) were separated using a capillary column (PLOT Al$_2$O$_3$ 50 m × 0.53 mm). The GC oven temperature was initially set to 30°C for 10 min, and then increased to 180°C at 10°C/minute and held at this temperature for 20-30 min. Compound specific stable carbon isotope ratios were determined by Finnigan Mat Delta Plus mass spectrometer interfaced to a HP 5890II gas chromatograph. Gas components were separated on the GC using helium as the carrier gas, converted into CO$_2$ in a combustion interface, and then introduced into the mass spectrometer. Individual hydrocarbon gas components (C$_1$-C$_5$) and CO$_2$ were initially separated using a fused silica capillary column (PLOT Q 30m × 0.32 mm). The GC oven temperature was increased from 35°C to 80°C at 8°C/min, then to 260°C at 5°C/min, and held there for 10 min. Stable isotope ratios for carbon are reported in δ notation in per mil (‰) relative to VPDB. The measurement precision was estimated to be ±0.5‰ for δ$^{13}$C. When chemical compositions and compound specific stable carbon isotope ratios for the gas sample of each step were determined, the corresponding characteristics of the whole desorption gas for each core sample were calculated.

3. Results and discussion

3.1. Origin of hydrocarbon gases

The hydrocarbons in natural gases are believed to come from two sources, biogenic and thermogenic, which can be inferred via the carbon isotope composition and molecular composition of hydrocarbon gases [5]. Biogenic gas commonly has δ$^{13}$C$_{methane}$ less than -60‰ and high content of methane [5]. Thermogenic gas is generally characterized by dryness < 99% and δ$^{13}$C$_{methane}$ > -50‰ [9]. The hydrocarbon gases composition and carbon isotope composition of the desorption gases for shale samples were listed in Table 1. The hydrocarbon gases in the desorption gases of the studied shale samples are dominated by methane, the content of which ranges from 23.33% to 35.73% with an average of 29.98%. Ethane also has a relatively high content, which ranges from 2.65% to 20.34% with a mean value of 14.22%. The composition of hydrocarbon gases decreases with the increasing of carbon number. The dryness coefficient (C$_1$/C$_{total}$) of the desorption gases range from 0.45 – 0.82 with an average of 0.58. The δ$^{13}$C value for methane in the desorption gases range between −57.15‰ and −
53.71‰ with an average of –55.25‰, which for ethane and propane are –49.24‰ to –47.20‰ and –37.63‰ to –34.61‰ respectively. To better distinguish between biogenic and thermogenic origin for the desorption gases, the diagram of the hydrocarbon gas component ratio \( C_1/C_{2+3} \) versus \( \delta^{13}C_{\text{methane}} \) (Figure 1, after [10]) was used in this study. The molecular and isotope compositions of the desorption gases region in the mixing area and are close to thermogenic origin characteristic, which indicate that the desorption gases generally derived from a mixed origin with primary contribution from thermogenic processes.

Table 1. The hydrocarbon gases composition and carbon isotope composition of the desorption gases.

| Sample | Gas composition (%) | \( C_1/C_{2+3} \) | \( \delta^{13}C \) (‰) |
|--------|---------------------|-----------------|-----------------|
| YK-230.1 | CH₂ 35.73  | C₂H₆ 20.34 | C₃H₈ 11.56 | iC₄H₁₀ 0.70 | nC₄H₁₀ 2.85 | iC₅H₁₂ 0.33 | nC₅H₁₂ 0.91 | C₁/C₇ 0.49 | \( \delta^{13}C_4 \) -53.71 | \( \delta^{13}C_{2+3} \) -48.67 | \( \delta^{13}C_{3} \) -37.15 |
| YK-234.8 | CH₂ 27.33  | C₂H₆ 13.80 | C₃H₈ 7.45 | iC₄H₁₀ 0.46 | nC₄H₁₀ 1.76 | iC₅H₁₂ 0.12 | nC₅H₁₂ 0.72 | C₁/C₇ 0.53 | \( \delta^{13}C_4 \) -55.42 | \( \delta^{13}C_{2+3} \) -48.46 | \( \delta^{13}C_{3} \) -36.24 |
| YK-237.3 | CH₂ 33.53  | C₂H₆ 20.08 | C₃H₈ 12.70 | iC₄H₁₀ 0.78 | nC₄H₁₀ 3.13 | iC₅H₁₂ 0.39 | nC₅H₁₂ 0.77 | C₁/C₇ 0.45 | \( \delta^{13}C_4 \) -54.70 | \( \delta^{13}C_{2+3} \) -49.24 | \( \delta^{13}C_{3} \) -37.63 |
| YK-340.7 | CH₂ 23.33  | C₂H₆ 2.65 | C₃H₈ 1.68 | iC₄H₁₀ 0.33 | nC₄H₁₀ 0.42 | iC₅H₁₂ 0.08 | nC₅H₁₂ 0.08 | C₁/C₇ 0.82 | \( \delta^{13}C_4 \) -57.15 | \( \delta^{13}C_{2+3} \) -47.20 | \( \delta^{13}C_{3} \) -34.61 |

It should be noticed that dryness coefficient for desorption gas of YK-340.7 (0.82) is remarkable higher than which of other samples (0.45 – 0.53). The ratio of \( (iC₄H₁₀ + iC₅H₁₂) / (nC₄H₁₀ + nC₅H₁₂) \) for the former (0.81) is also higher than which for the latter (0.23 – 0.30). Biodegradation could affect molecular and isotope composition of natural gas. It is generally believed that methane is more difficult to activate than larger alkanes in the biodegradation process, and butane and pentane are more preferable for biodegradation than iso-butane and iso-pentane [11]. Besides, positive deviation of \( \delta^{13}C \) is an indicator for biodegradation, for heavier isotope \( (^{13}C \) is discriminate by the involved enzymes [12]. The \( \delta^{13}C_2 \) and \( \delta^{13}C_3 \) for desorption gas of YK-340.7 are heavier than which of other samples (Table 1), combining with gas composition characteristic mentioned above, indicate that shale gas in YK-340.7 could experience biodegradation.

Figure 1. \( C_1/(C_2+C_3) \) versus \( \delta^{13}C_{\text{methane}} \) for desorption gases of lacustrine shale samples (after [10])

3.2. Gas characteristics variation during desorption process

In this study, the desorption process for gas in the studied shale samples could be divided into two parts according to the desorption temperature: desorption at ambient temperature (part A) and
desorption under heating (part B). The hydrocarbon gases desorbed in part A are dominated by methane, the relative composition of which range from 70.4% to 93.3% and show a week declining trend with increasing desorption time. In contrast, the relative composition of ethane and propane show week increasing trends. The dryness coefficient of hydrocarbon gases desorbed in part A range from 0.70 to 0.93 (Figure 2). The relative composition of methane desorbed in part B are much lower than which desorbed in part A, show a significant declining trend with increasing desorption temperature. The relative composition of methane even lower than which of ethane and propane in the desorption step with temperature of 80 °C for sample YK-230.1 and YK-237.3. The dryness coefficient of hydrocarbon gases desorbed in part B (range from 0.20 to 0.87) also decrease significantly with increasing desorption temperature (Figure 2). The adsorption affinities of hydrocarbon gases increase with the increasing carbon number [13]. Hydrocarbon gas with week adsorption affinities, such as methane, desorb preferentially in desorption process, leading to a dominated composition in hydrocarbon gases of initial period of desorption process. With the desorption processing, the amount of adsorbed methane decreases more rapidly than hydrocarbon C_{2+}, leading to a less content in late period of desorption process. Dry coefficient of desorbed gases for all steps of YK-340.7 (0.68 – 0.93) are remarkable higher than which of other samples (0.20 – 0.76), which is caused by biodegradation, as discussed above.

![Figure 2](image.png)

**Figure 2.** The relative composition of hydrocarbon gases variation during desorption process

The δ^{13}C_{methane} value for the desorbed gases of every steps shows a wide variation from −63‰ to −49.6‰. A general enrichment of δ^{13}C in methane was observed in the whole desorption process except the first step of heating desorption, in which the δ^{13}C_{methane} value shows a decrease comparing with which of the last step of desorption at ambient temperature (Figure 3). Changes in the δ^{13}C_{ethane} value are much less significant, the range of which is −49.6‰ to −44.6‰. Variations for the δ^{13}C_{propane} value of desorbed gases for sample YK-230.1 and YK-234.8 are week too, but for which of sample YK-237.3 and YK-240.7, slight decrease trends are observed in desorption process. The differences in molecular mobility (effective diffusion coefficients) of the ^{12}CH_{4} and ^{13}CH_{4} lead to a significant
depletion of $^{13}\text{C}$ in the gas diffusion process in shale [7], which should be the main reason for variation of the $\delta^{13}\text{C}_{\text{methane}}$ value during desorption process observed in this study. The effect of $^{13}\text{C}$ for molecular mobilities of propane in shale could be more complicated, then lead to various changes in the $\delta^{13}\text{C}_{\text{propane}}$ value during desorption process. The carbon isotopic ratio of hydrocarbons in desorbed gases show general trends of $\delta^{13}\text{C}_{\text{methane}} < \delta^{13}\text{C}_{\text{ethane}} < \delta^{13}\text{C}_{\text{propane}}$, but difference between $\delta^{13}\text{C}_{\text{methane}}$ and $\delta^{13}\text{C}_{\text{ethane}}$ decline with increasing degree of desorption. In the desorption step under 80 °C for sample YK-237.3, difference between $\delta^{13}\text{C}_{\text{methane}}$ and $\delta^{13}\text{C}_{\text{ethane}}$ is only –0.3‰. The carbon isotope reversal of hydrocarbon gases in shale gas has been reported [14]. The findings of this study indicate that $^{13}\text{C}$ fractionation during desorption process could be a possible reason for carbon isotope reversal of shale gas.

![Figure 3](image)

**Figure 3.** The carbon isotopic composition for hydrocarbon variation during desorption process

4. Conclusions

Desorption gases of four lacustrine shallow shale cores from the Triassic Yanchang formation of the Ordos Basin, China were collected, and their molecular and carbon isotope compositions were analyzed in this study. Results show that hydrocarbon gases of desorption gas are dominated by methane with relatively low dryness coefficient ranging from 0.45 to 0.82. The $\delta^{13}\text{C}$ values for hydrocarbon gases increase with increasing carbon number, and which for methane ranges from $-57.15$‰ to $-53.71$‰. The hydrocarbon gases generally derived from a mixed origin with primary contribution from thermogenic processes. Desorption gases of sample YK-340.7 could experience biodegradation for its relatively high dryness coefficient and $(i\text{C}_{4}H_{10} + i\text{C}_{5}H_{12}) / (n\text{C}_{4}H_{10} + n\text{C}_{5}H_{12})$ value. A significant depletion of $^{13}\text{C}$ for methane was observed during desorption process, the reason for which could be differences in molecular mobility of the $^{12}\text{C} \text{H}_4$ and $^{13}\text{C} \text{H}_4$. Changes in the $\delta^{13}\text{C}_{\text{ethane}}$ and $\delta^{13}\text{C}_{\text{propane}}$ during desorption process are week.

Acknowledgements
This research was financially supported by “Light of West China” Program of the Chinese Academy of Sciences, the Key Laboratory Project of Gansu Province (Grant No. 1309RTSA041), the National Nature Science Foundation of China (Grant No. 41402128) and National Science and Technology Major Project (Grant No. 2016ZX05003002).

References

[1] Schettler P D and Parmely C R 1990 The measurement of gas desorption isotherms for Devonian shale Gas. Shales Technol. Rev. 7 4–9.

[2] Jarvie D M, Hill R J, Ruble T E and Pollastro R M 2007 Unconventional shale-gas systems: The Mississippian Barnett Shale of north-central Texas as one model for thermogenic shale-gas assessment AAPG Bull. 91 475–499.

[3] Martini A M, Walter L M, Budai J M, Ku T C W, Kaiser C J and Schoell M 1998 Genetic and temporal relations between formation waters and biogenic methanedUpper Devonian Antrim Shale, Michigan basin, USA Geochim. Cosmochim. Acta 62 1699–1720.

[4] Osborn S G and McIntosh J C 2010 Chemical and isotopic tracers of the contribution of microbial gas in Devonian organic-rich shales and reservoir sandstones, northern Appalachian Basin Appl. Geochem. 25 456–471.

[5] Schoell M 1983 Genetic characterization of natural gas AAPG Bull. 67 2225–2238.

[6] Xia X and Tang Y 2012 Isotope fractionation of methane during natural gas flow with coupled diffusion and adsorption/ desorption Geochem. Cosmochim. Acta 77 489–503.

[7] Zhang T and Krooss B M 2001 Experimental investigation on the carbon isotope fractionation of methane during gas migration by diffusion through sedimentary rocks at elevated temperature and pressure Geochem. Cosmochim. Acta 65 2723–2742.

[8] Li J, Zhou S, Li Y, Ma Y, Yang Y and Li C 2016 Effect of organic matter on pore structure of mature lacustrine organic-rich shale: A case study of the Triassic Yanchang shale, Ordos Basin, China Fuel 185 421-431

[9] Jenden P D, Drazan D J and Kaplan I R 1993 Mixing of thermogenic natural gases in northern Appalachian Basin AAPG Bull. 77 980–998.

[10] Golding S D, Boreham C J and Esterle J S 2013 Stable isotope geochemistry of coal bed and shale gas and related production waters: A review Int. J. Coal Geol. 120 24–40.

[11] Welte D H, Kratochvil H, Rullkötter J, Ladwein H, and Schaefer R G 1982 Organic geochemistry of crude oils from the Vienna Basin and an assessment of their origin Chem. Geol. 35 33–68.

[12] Kinnaman F S, Valentine D L and Tyler S C 2007 Carbon and hydrogen isotope fractionation associated with the aerobic microbial oxidation of methane, ethane, propane and butane Geochem. Cosmochim. Acta 71 271–283.

[13] Chen Y, Qin Y, Luo Z, Yi T, Wei C, Wu C and Li G 2019 Compositional shift of residual gas during desorption from anthracite and its influencing factors Fuel 250 65–78.

[14] Zumberge J E, Ferworn K A and Brown S 2012 Isotopic reversal(‘rollover’) in shale gases produced from the Mississippian Barnett and Fayetteville formations. Mar. Pet. Geol. 31 43–52.