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The origin and evolution of thermogenic gases in organic-rich marine shales



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ABSTRACT

In order to better understand the generation and primary source of mature thermogenic gas in shale, and to evaluate the residual gas generation potential of the shale at different maturity levels, we performed pyrolysis experiments on an organic-rich marine shale and its kerogens prepared by artificial maturation. The results indicate that the thermal maturation of organic matter in the shale can be divided into four stages: oil generation ($< 0.6\text{--}1.0\%$ EasyRo), condensate generation ($1.0\text{--}1.5\%$ EasyRo), wet gas generation ($1.5\text{--}2.2\%$ EasyRo), and dry gas generation ($2.2\text{--}4.5\%$ EasyRo). Thermogenic methane is produced mainly during wet gas and dry gas generation, while most of the C_{2+} hydrocarbon gases are produced during condensate and wet gas generation. The kerogen at a thermal maturity of $> 3.0\%$ EasyRo still has methane generation potential. Whether or not gas generation potential of a highly mature kerogen has a commercial significance depends on its organic matter richness, thermal maturity internal and some other geological factors, such as caprock sealing property, reservoir physical property, and tectonic movement. In addition to the gas produced from kerogen cracking, gas is also generated from the secondary cracking of residual bitumen as maturation progresses. Early hydrocarbon expulsion during oil generation likely has a considerable effect on the amount and $\delta^{13}\text{C}$ values of the late-generated shale gas. The lower the oil expulsion efficiency of a shale, i.e., the more retained bitumen, then the higher the productivity of post-mature shale gas and comparative enrichment of the latter in ^{12}C .

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1. Introduction

Hydrocarbon generation potential is commonly assessed by the abundance, type, and thermal maturity of organic matter in source rocks. Productive shale gas formations in North America generally have $> 2.0\%$ TOC, type II kerogen, and $> 1.3\%$ (vitrinite reflectance equivalent) thermal maturity (Zumberge et al., 2012). However, the geological settings of organic-rich, marine shale formations in China are distinct from those in North America. In China, shale gas formations are characterized by old strata, deep burial, high thermal maturity, and multi-stage tectonism (Dai et al., 2014; Zou et al., 2015). Therefore, more targeted criteria are needed to evaluate shale gas generation potential in China. Investigations into the origin and formation mechanism of highly mature and over-mature shale gas, the upper limit of maturation for gas generation from marine kerogens, and the effect of intense tectonism on the deformation and alteration of shale gas reservoirs are more critical for Chinese shale gas exploration.

Shale gas is natural gas trapped within shale, which has biogenic and thermogenic origins (Martini et al., 1998; Jarvie et al., 2007). The sources of thermogenic gas in shale include kerogen (insoluble organic matter), bitumen (soluble organic matter), and often pyrobitumen (a residue of bitumen cracking) (Jarvie et al., 2007) (Fig. 1). Different gas generation stage and gas generation potential result in the changes of their relative contributions to shale gas with thermal maturation. For example, during early maturation, little gas is produced together with the formation of bitumen, and the gas is derived mainly from the primary cracking of kerogen. With increasing maturity, bitumen (as the intermediate of kerogen cracking) becomes an important source of gas. During late maturation, a large amount of gas is produced from the cracking of both kerogen and bitumen. Because kerogen does not migrate out of the source rock, its contribution to gas generation is relatively stable and simple to evaluate. On the other hand, the gas contribution of bitumen depends on the hydrocarbon expulsion efficiency of shale (Fig. 1). The cracking of oil, or expelled bitumen, is considered the major source of conventional gas generated from hydrogen-rich marine source rocks (Welte et al., 1988; Rooney et al., 1995). Conventional and unconventional gas fields commonly occur together within a hydrocarbon basin (Zou et al.,

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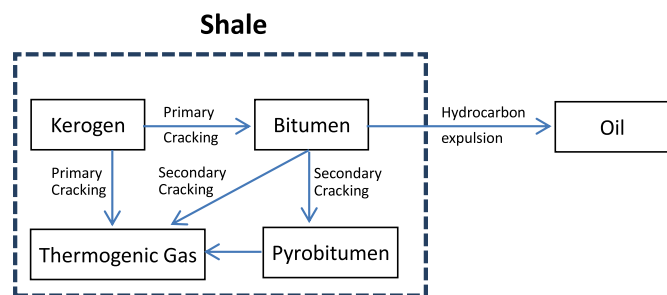


Fig. 1. Process of the indigenous generation of thermogenic gas in shale (modified from Jarvie et al., 2007).

2015), where the cracking of expelled oil produces conventional gas, and the cracking of retained oil (i.e., bitumen) and kerogen generates unconventional gas. As more oil is expelled, less bitumen is retained in the shale to generate unconventional gas. Therefore, high hydrocarbon expulsion efficiency at peak oil generation is favorable for the generation of conventional gas, but unfavorable for the generation of unconventional gas.

At present, no method can effectively determine the hydrocarbon expulsion efficiency of source rocks. The simulation of hydrocarbon expulsion under actual geological conditions is also difficult. Gai et al. (2015) used an artificial mix of kerogen and its extracts to design a suite of samples with variable oil expulsion efficiencies, and performed pyrolysis experiments to analyze the effect of oil expulsion efficiency on shale gas generation in a closed system. During shale maturation, however, bitumen is an intermediate product with an evolving concentration, composition, and gas generation potential. Thus, hydrocarbon expulsion is a dynamic process, and its contribution to gas generation depends on thermal maturity.

The purpose of this study was to improve our understanding of the generation mechanisms of, and precursors to, shale gas in mature organic-rich marine shale, and to evaluate the effect of hydrocarbon expulsion on shale gas potential. A series of laboratory simulations was performed on a marine shale and its kerogens using artificial maturation. The pyrolysis of the source rock and its original kerogen was used to simulate the generation of shale gas in a closed system. The combination of artificial maturation and closed gold tube pyrolysis was used to obtain the residual gas generation from kerogens at various levels of thermal maturity.

2. Experimental methods

2.1. Samples

The marine shale sample used in this study was collected from the upper Proterozoic Xiamaling Formation in the Xiahuayuan region of Zhangjiakou City, Hebei Province, China. The geochemical characterization of the Xiamaling Formation in this area had been described by Zhang et al. (2007). This shale contains type II kerogen with a low T_{max} value of 434 °C, a vitrinite-like maceral reflectance (Ro) value of 0.57%, and a relatively high TOC content of 6.78 wt%. Prior to analysis, the surface of the sample was cleaned with dichloromethane, and the shale was ground to 100 mesh. We performed a sealed gold tube pyrolysis experiment on the shale to simulate the generation of shale gas and to assess its maximum gas yield.

The source rock sample was demineralized in a water bath (80 °C) with hydrochloric and hydrofluoric acids to isolate kerogen that was then ground to 100 mesh. The kerogen concentrate was Soxhlet-extracted for 72 h with dichloromethane:methanol

Table 1

Conditions for the preparation of kerogen samples used in the simulation experiments.

Kerogen	Maturity (% EasyRo)	Heating temperature (°C)	Heating time (h)	Residual rate (%) ^a	TOC (wt%)
K ₁	0.57	–	–	100	68.12
K ₂	0.80	320	57	85.7	73.77
K ₃	1.0	345	65	82.4	69.92
K ₄	1.3	365	95	77.2	72.56

^a The ratio is calculated by kerogen mass before and after heating

(93:7 v/v) to remove soluble organic matter, and was then dried at 50 °C for 12 h. This kerogen represents the original kerogen before oil generation (K₁). The other three kerogen samples (K₂, K₃, and K₄) were prepared by artificial maturation of the original kerogen (K₁) over the full thermal range of oil generation. The artificial maturation process was performed in a vacuum glass tube. Heating temperature and times were based on the EasyRo method of Sweeney and Burnham (1990) (Table 1). The kerogen was Soxhlet-extracted with dichloromethane for 72 h to remove newly produced soluble organic matter, and was used to simulate the formation of gas from kerogen cracking at various stages of maturation.

2.2. Pyrolysis experiments

Pyrolysis experiments on the marine shale (whole rock) and four extracted kerogens representing four stages of maturation (0.57% VRo, 0.80%, 1.0%, and 1.3% EasyRo) were carried out in sealed gold tubes following Xiong et al. (2004). Aliquots of 10–50 mg kerogen or 50–100 mg whole-rock shale were loaded into gold tubes (40 mm length, 4.2 mm inside diameter, and 0.25 mm wall thickness) before being purged with argon for 5 min and sealed under an argon atmosphere. The sealed gold tubes were placed in stainless steel autoclaves that were heated in an oven at two constant heating rates of 20 °C/h and 2 °C/h, under constant pressure of 50 MPa. Sampling was conducted at ca. 24 °C intervals between 336 °C and 600 °C (12 total samples for each heating rate). After heating, the autoclaves were removed from the oven and cooled to room temperature.

2.3. Determination of pyrolytic products

The pyrolysates were analyzed to determine the chemical and carbon isotopic compositions of gaseous hydrocarbons using gas chromatography (GC) and gas chromatography–isotope ratio mass spectrometry (GC–IRMS). The cleaned gold tube for each temperature point was placed in a vacuum glass system connected to a GC inlet. After piercing the gold tube with a steel needle, the gaseous components were released and introduced into the GC system, where they were quantified using an Agilent Technologies 7890-0322 GC. The system had high sensitivity (as good as for the analysis of 0.01 mL volume of gas), good accuracy (with the relative errors being less than 0.5%). The analysis of all gaseous hydrocarbons (C₁–C₅) and other gas components (such as N₂, H₂ and CO₂) could be carried out with a single injection. The carbon isotopic compositions of gaseous hydrocarbons were determined on a GV Instruments Isoprime stable isotope mass spectrometer. Reported isotopic data represented the arithmetic means of at least two duplicate analyzes, and the repeatability was less than 0.3‰. All carbon isotopic values were reported in per mil (‰) relative to the VPDB standard.

The gold tube for the analysis of C₆–C₁₂ hydrocarbons was cooled for about 30 min using liquid nitrogen, and then rapidly cut in half and placed in a 4 mL vial filled with methanol. The C₆–C₁₂

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