Geological Openness Effect on the Chemical and Carbon Isotopic Signatures of Shale Gas: Implications from the Stepwise Pyrolysis Bitumen

Hui Tian¹, Haifeng Gai¹, Tongwei Zhang², Xianming Xiao¹, and Baojia Huang³

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Abstract

Earlier studies have revealed that part of shale gas is derived from the cracking of residual oils, and one line of evidence of this process is the presence of abundant pyrobitumen in mature and over-mature gas shales. Many experiments have been carried out to investigate the chemical and carbon isotopic signatures of oil cracking gas in a closed or confined system, but most of the results failed to fully explain the characteristics of shale gas that is usually much drier and characterized with relatively heavier methane carbon isotopes than the pyrolysate gas. In fact, the shale system is probably not a completely closed or confined system when the shale gas is being generated, and therefore the shale gas could be released periodically with the natural fracturing of shales induced by gas generation. This overpressure fracturing has been recorded by the fluid inclusions of gas in some gas shales. From this point of view, the shale gas today may be considered as the residual part of more abundant gas generated in shales. Therefore, it is necessary to carry out experiments that can match the geological conditions as much as possible.

In this study, we performed a series of closed and stepwise experiments on a low mature bitumen (Rb=0.8%) using sealed gold tube method to investigate how the experimental openness affected the chemical composition of pyrolysates, the methane yield and its carbon isotope. The closed experiment shows that most of the ethane and propane is generated before the maturity level of EasyRo 2.3% and 1.7%, respectively. In the stepwise experiments, the residual bitumen samples that have been artificially depleted of ethane and propane potentials, were pyrolyzed again to imitate the regeneration of gas after shale fracturing and subsequent gas loss, and to investigate the late methane potential and its carbon isotopic composition without the influence of ethane and propane. The results show that there is still a maximum methane potential of about 70-102 mL/g bitumen, and the methane carbon isotopic values are 3-5‰ heavier than those in the closed system and are much closer to the carbon isotopes of methane in shale gases. These results imply that (1) the cracking of wet gases in a closed system will produce isotopically lighter methane than the cracking of residual bitumen itself, and (2) the shale gas today is only the residual part of gas generated in shales after its migration into conventional reservoirs.
Selected References


Geological Openness Effect on the Chemical and Carbon Isotopic Signatures of Shale Gas: Implications from Stepwise Pyrolysis of a Low Mature Bitumen Sample

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Why geological openness and why bitumen?

Stepwise pyrolysis experiments

What can we learn?
- Gas potential
- Chemical and isotopic signatures
- Geological implications

Summary
Presenter’s notes: Overpressure by oil cracking can be recorded by pure methane inclusion. The Raman shift has been used to infer the density or internal pressure of methane in fluid inclusion.
**Why geological openness?**

**How different are the gases from kerogen and oil cracking?**

For confined or closed geological systems:
- Kerogen cracking gas is much wetter than oil cracking gas
- Wet gas contribution to late methane is more profound for oil cracking gas

Presenter’s notes: Most methane from oil cracking is derived from the secondary of wet gases at highly maturity level. Without wet gas contribution, late methane from oil cracking might be very low.
Presenter’s notes: Primary migration of oils out of shales leaves the retained oil more asphaltene riched than the oils accumulated in conventional reservoirs.

Oil cracking gas in shales might be largely sourced from resin and asphaltene fractions.
Presenter’s notes: Conventionally, carbon isotopic composition for partially trapped methane is estimated from the Rooney model on the basis of mass balance. This model, however, applies well to a simple situation where the methane is generated from a single source. For methane from oil cracking gas, its source is very complex, and the methane carbon isotope for partially trapped methane may be significantly distorted using the Rooney model.
Experimental design

Bitumen sample

TOC: 80.9%; EqvRo≈0.8; stable carbon isotope: -35.7‰

<table>
<thead>
<tr>
<th>Pyrolysis Temp (°C)</th>
<th>EasyRo (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Original</td>
<td>0.80</td>
</tr>
<tr>
<td>480</td>
<td>1.81</td>
</tr>
<tr>
<td>500</td>
<td>2.12</td>
</tr>
<tr>
<td>510</td>
<td>2.30</td>
</tr>
<tr>
<td>530</td>
<td>2.65</td>
</tr>
<tr>
<td>600</td>
<td>3.88</td>
</tr>
</tbody>
</table>

Pyrolysis program:
- 12 h from room temperature to 200 °C;
- 20 °C/h from 200 °C to 600 °C

Max. EasyRo=3.88%
Experimental setup

- Gold tubes
- Argon welder
- Autoclave
- Pressure lines
- Oven
- TC
Gas potential

Comparison of intermittently open and constantly confined systems

Geological openness affects TOC/bitumen criteria for potential gas shales!

Comparison of gas potential:
- 1 wt.% for cumulative gas
- 8 wt.% for partially trapped gas after EasyRo=2.65%

Gas potential is calculated as the total volume of C$_1$–C$_5$ at STP conditions (0 °C and 1 atm)
Using data from a constantly confined system to estimate gas potential for an intermittently open system could overestimate the gas potential.

Gas potential could be significantly overestimated by extrapolating data from a constantly confined system to an intermittently open system!
Gas potential

Mass balance for an intermittently open system

With system breaking up, the total gas volume generated from bitumen never exceeds that from a constantly confined system when the bitumen reached to the same thermal maturity level!
Late gas from bitumen itself rather than wet gas cracking is dry with gas wetness values comparable to those observed for natural gases in thermally over-mature shales!
Stable carbon isotopes

Trapping efficiency significantly affects methane and ethane carbon isotopes, but no reversals were observed!

Constantly confined system
Stable carbon isotopes

CO₂ in natural shale gas may have been involved in reactions to form isotopically light ethane

(Tang et al., 2011; Zumberge et al., 2012)

Primitive organic CO₂ are isotopically light

Dai et al., 2016, Marine and Petroleum Geology

Constantly confined system

matured to EasyRo=3.88%  matured to EasyRo=3.2%

Original, 1.81, 2.12, 2.3, 2.65
Geological implications

Methane carbon isotope fractionation at EasyRo = 3.88%
in a constantly confined system for various gas sources

<table>
<thead>
<tr>
<th>Organic type</th>
<th>Bulk $\delta^{13}C$ (‰)</th>
<th>$\delta^{13}C_1$ (‰) *</th>
<th>Difference (‰)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Marine whole oil</td>
<td>-28.6</td>
<td>-34.8</td>
<td>6.2</td>
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<tr>
<td>Saturates</td>
<td>-28.5</td>
<td>-35.5</td>
<td>7</td>
</tr>
<tr>
<td>Aromatics</td>
<td>-28.3</td>
<td>-32.2</td>
<td>3.9</td>
</tr>
<tr>
<td>Asphaltenes</td>
<td>-28.4</td>
<td>-33.1</td>
<td>4.7</td>
</tr>
<tr>
<td>Solid bitumen</td>
<td>-35.7</td>
<td>-38.7</td>
<td>3</td>
</tr>
<tr>
<td>Mature type II kerogen</td>
<td>-30.4</td>
<td>-31.5</td>
<td>1.1</td>
</tr>
</tbody>
</table>

*: matured to EasyRo = 3.88% in a constantly confined system

Methane carbon isotopes are expected to be variably lighter than the bulk carbon isotopes of their parent sources.
Geological implications

Very heavy methane carbon isotope values for oil/bitumen cracking gas

<table>
<thead>
<tr>
<th>Sample</th>
<th>Depth (m)</th>
<th>EqVRo (%)</th>
<th>CH₄ (%)</th>
<th>C₂H₆ (%)</th>
<th>C₂H₅ (%)</th>
<th>CO₂ (%)</th>
<th>N₂ (%)</th>
<th>δ¹³C₂ (%)</th>
<th>δ¹³C₃ (%)</th>
<th>δ¹³C₄ (%)</th>
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</thead>
<tbody>
<tr>
<td>Ning201-H1</td>
<td>2745</td>
<td>99.12</td>
<td>0.5</td>
<td>0.01</td>
<td>0.04</td>
<td>0.3</td>
<td>-27</td>
<td>-34.3</td>
<td>-34.1</td>
<td>-34.5</td>
</tr>
<tr>
<td>Ning201-H1</td>
<td>2745</td>
<td>99.04</td>
<td>0.54</td>
<td>0.4</td>
<td>0</td>
<td>0</td>
<td>-27.8</td>
<td>-33.8</td>
<td>-34.1</td>
<td>-34.5</td>
</tr>
<tr>
<td>Ning211</td>
<td>2313-2341</td>
<td>3.2</td>
<td>98.53</td>
<td>0.32</td>
<td>0.03</td>
<td>0.91</td>
<td>0.17</td>
<td>-28.4</td>
<td>-33.8</td>
<td>-36.2</td>
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<tr>
<td>Ning312-1</td>
<td>2790</td>
<td>99.07</td>
<td>0.42</td>
<td>0.1</td>
<td>0</td>
<td>0.4</td>
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<td>-33.8</td>
<td>-34.1</td>
<td>-35.4</td>
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<tr>
<td>Ning312-2</td>
<td>2586</td>
<td>99.28</td>
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<td>0.01</td>
<td>0</td>
<td>0.23</td>
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<td>-34</td>
<td>-35.5</td>
<td>-35.9</td>
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<tr>
<td>Ning312-3</td>
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<td>98.62</td>
<td>0.42</td>
<td>0.01</td>
<td>0.59</td>
<td>0.37</td>
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<td>-35.5</td>
<td>-36.2</td>
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<td>Ning312-4</td>
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<td>0</td>
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<tr>
<td>Zhao104</td>
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<td>99.25</td>
<td>0.52</td>
<td>0.01</td>
<td>0.07</td>
<td>0.15</td>
<td>-26.7</td>
<td>-31.7</td>
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<tr>
<td>YSL1-1H</td>
<td>2002-2028</td>
<td>3.2</td>
<td>99.45</td>
<td>0.47</td>
<td>0.01</td>
<td>0.01</td>
<td>0.03</td>
<td>-27.4</td>
<td>-31.6</td>
<td>-33.2</td>
</tr>
</tbody>
</table>

Dai et al., 2016, Marine and Petroleum Geology

Shale gases with very high maturity were not generated in a constantly confined system

Presenter’s notes: Compared with the carbon isotopes of kerogen, the carbon isotopes for methane are abnormally heavy, indicating they are partially trapped or are regenerated from residual bitumen with very high thermal maturity.
Geological implications

Very heavy methane carbon isotope values for oil/bitumen cracking gas

System breaking up might lead to much heavier methane carbon isotopes than a constantly confined system!

Values may be variable depending on specific parent sources!
Geological implications

A higher but not impossible bitumen or TOC content is needed to reach a minimum gas content of 2 m$^3$/ton for industrial production.

Sufficient gas potential can also be achieved even if system breaks up at a high maturity level.

The gas wetness values are comparable to those observed for naturally produced shale gas.
Summary

- For an intermittently open shale reservoirs, a higher TOC content is required to generate sufficient dry gas with isotopically heavy methane, but no carbon isotopic reversals were observed during pyrolysis experiments.

- Primitive organic CO$_2$ generated in pyrolysis experiments are isotopically lighter than the CO$_2$ in natural shale gases, confirming that CO$_2$-involved reactions to form isotopically light ethane or butane that leads to carbon isotope reversals (Tang et al., 2011; Zumberge et al., 2012);

- Specific pyrolysis experiments are recommended for given shale gas plays to fully understand their shale gas potential and geochemical characteristics.
Thanks for your time!
Any questions?