Experimental Gas Extraction by Rock Crushing: Evidence for Preservation of Methane in Core Samples from the Mudstones of the Eagle Ford Formation and Barnett Shales*

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Abstract

Accurately determining oil-in-place (OIP) and gas-in-place (GIP) is critical for evaluating shale oil and gas plays. Methane is typically stored in nano-size pores in low permeability mudstones, but many of these hydrocarbon-saturated pores may isolate from surrounding mineral matrix. A rock crushing experiment has been devised to test for the presence of gas and condensate in isolated nanopores. We utilize a gas-tight rock crushing cell that can directly introduce released gas to a gas chromatograph after crushing. We have tested this method on mudstones of the Upper Cretaceous Eagle Ford Formation, an emerging oil/gas shale play in the Maverick Basin and the adjacent San Marcos Arch of South Texas.

Five core samples (depths: 4,758ft to 13,608 ft) were collected from the organic matter-rich lower Eagle Ford unit and used in our study. TOC content and Tmax values range from 1.8% to 8.5%, and 428°C to 543°C, respectively. Calculated Ro, based on Tmax, ranges from 0.5% to 2.6%. Hydrogen index (HI) ranges from 741mgHC/g TOC at Ro of 0.5% to 14 mgHC/g TOC at Ro > 1.6%. The large decrease in HI value with increasing thermal maturity results from the transformation of organic matter to oil and gas. CH₂Cl₂ extractable hydrocarbons show that the ratio of the sum of C₈-C₁₄ to the sum of C₁₅-C₃₂ increases with thermal maturity. The above geochemical observation clearly suggests that oil properties in the organic-rich lower Eagle Ford unit are closely related to thermal maturation of organic matter.

CH₄/CO₂ ratios of gases released during crushing are lower at low thermal maturities and higher at high maturities because more CH₄-rich gas is generated at high maturity levels. CH₄/CO₂ ratios decrease with longer rock crushing time because of the increase in the CO₂-rich adsorbed-gas contribution. Both thermal maturity and gas desorption contribute to changes in CH₄/CO₂ ratio of gas released from rock crushing. However, no obvious compositional fractionation occurs among C₁, C₂ and C₃ during rock crushing. C₁/C₂ and C₂/C₃ ratios remain constant through crushing but greatly increase when the level of thermal maturity is high. Geochemical parameters (C₁/C₂, iC₄/nC₄) of gas released during rock crushing are good indicators of thermal maturation of organic-rich shales. CH₄/CO₂ ratio is a good indicator of free gas and adsorbed gas contributions.
References


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The Bureau of Economic Geology
The University of Texas at Austin
General Scheme of Hydrocarbon Formation with Source Rock Burial

(Tissot and Welte, 1978)
Questions

• What are main controlling factors of gas chemistry in shale gas systems?

• What differences exist between gases produced from kerogen primary cracking and secondary oil cracking?

• What are the main gas storage components: free gas vs. adsorbed gas?

• How does mineral matrix affect gas storage?

• Are major gas storage components predictable by integrating gas chemistry and rock properties?
Eagle Ford Core Gas Data

- Tesoro Hendershot #1
- Getty Hurt #1
- Shell Hay #1
- Shell Leppard #1
- Shell Roessler #1
# Eagle Ford Core Geochemistry Data

For a Range of Thermal Maturities

<table>
<thead>
<tr>
<th>Well parameters</th>
<th>Hendershot #1</th>
<th>Getty Hurt #1</th>
<th>Shell Hay #1</th>
<th>Shell Leppard #1</th>
<th>Shell-Roessler #1</th>
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</thead>
<tbody>
<tr>
<td>Depth (ft)</td>
<td>4758</td>
<td>7298</td>
<td>13825</td>
<td>13827</td>
<td>13608</td>
</tr>
<tr>
<td>TOC</td>
<td>8.5</td>
<td>1.8</td>
<td>5.3</td>
<td>2.26</td>
<td>5.0</td>
</tr>
<tr>
<td>S1</td>
<td>1.8</td>
<td>1.2</td>
<td>1.8</td>
<td>0.83</td>
<td>0.2</td>
</tr>
<tr>
<td>S2</td>
<td>63.2</td>
<td>3.6</td>
<td>1.4</td>
<td>0.72</td>
<td>0.7</td>
</tr>
<tr>
<td>S3</td>
<td>1.0</td>
<td>0.3</td>
<td>0.4</td>
<td>0.32</td>
<td>0.3</td>
</tr>
<tr>
<td>S2/S3</td>
<td>63</td>
<td>12</td>
<td>3.4</td>
<td>2.25</td>
<td>3</td>
</tr>
<tr>
<td>S1/TOC</td>
<td>21</td>
<td>86</td>
<td>33</td>
<td>37</td>
<td>4</td>
</tr>
<tr>
<td>Tmax (° C)</td>
<td>428</td>
<td>446</td>
<td>475</td>
<td>494</td>
<td>533</td>
</tr>
<tr>
<td>Ro(%)_calc</td>
<td>0.5</td>
<td>0.9</td>
<td>1.4</td>
<td>1.73</td>
<td>2.4</td>
</tr>
<tr>
<td>HI</td>
<td>741</td>
<td>201</td>
<td>27</td>
<td>32</td>
<td>14</td>
</tr>
<tr>
<td>OI</td>
<td>12</td>
<td>17</td>
<td>8</td>
<td>14</td>
<td>5</td>
</tr>
<tr>
<td>PI</td>
<td>0.03</td>
<td>0.25</td>
<td>0.54</td>
<td>0.54</td>
<td>0.24</td>
</tr>
</tbody>
</table>
TIC of Solvent Extracts
Eagle Ford Core Samples

- Hendershot #1, Ro=0.5%
- Getty Hurt #1, Ro=0.9%
- Hay ED Unit #1, Ro=1.4%
- Shell Leppard 1, Ro=2.4%
- Getty Hurt #1, Ro=0.9%
- Hendershot #1, Ro=0.5%
Barnett Shale Core Gas Data

Sampled Cores
- 1=Lee C-5-1
- 2=Tarrant #A-3
- 3=Young #2
- 4=Sims #2
- 5=Blakely #1
# Barnett Core Geochemistry Data
## For a Range of Thermal Maturities

<table>
<thead>
<tr>
<th>Well Parameters</th>
<th>Brown, TX, LeeC-5-1</th>
<th>Jack, TX, Tarrant #A-3</th>
<th>Wise, TX Young #2</th>
<th>Wise, TX Sims #2</th>
<th>Wise, TX, Blakely #1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Depth (ft)</td>
<td>1250</td>
<td>6164</td>
<td>6168</td>
<td>6918</td>
<td>7634</td>
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<tr>
<td>TOC</td>
<td>7.88</td>
<td>7.05</td>
<td>3.27</td>
<td>4.50</td>
<td>3.64</td>
</tr>
<tr>
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<td>4.29</td>
<td>1.50</td>
<td>2.01</td>
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<tr>
<td>S2</td>
<td>20.24</td>
<td>14.74</td>
<td>4.07</td>
<td>2.86</td>
<td>1.07</td>
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<tr>
<td>S3</td>
<td>0.48</td>
<td>0.26</td>
<td>0.32</td>
<td>0.22</td>
<td>0.27</td>
</tr>
<tr>
<td>S2/S3</td>
<td>61</td>
<td>57</td>
<td>13</td>
<td>13</td>
<td>4</td>
</tr>
<tr>
<td>S1/TOC</td>
<td>37</td>
<td>61</td>
<td>46</td>
<td>45</td>
<td>10</td>
</tr>
<tr>
<td>Tmax (° C)</td>
<td>430</td>
<td>443</td>
<td>455</td>
<td>466</td>
<td>472</td>
</tr>
<tr>
<td>Ro(%)_calc</td>
<td>0.58(c)</td>
<td>0.81(c)</td>
<td>1.03(c)</td>
<td>1.23(c)</td>
<td>1.61(m)</td>
</tr>
<tr>
<td>HI</td>
<td>551</td>
<td>209</td>
<td>124</td>
<td>64</td>
<td>29</td>
</tr>
<tr>
<td>OI</td>
<td>9</td>
<td>4</td>
<td>10</td>
<td>5</td>
<td>7</td>
</tr>
<tr>
<td>PI</td>
<td>0.06</td>
<td>0.23</td>
<td>0.27</td>
<td>0.41</td>
<td>0.25</td>
</tr>
</tbody>
</table>
TIC of Solvent Extracts from Barnett Shale
Limitation of Methods in Hydrocarbon Characterization of Mudrocks

Ro(%)  0.5  0.8  1.2  2.0  2.5

Rock-Eval

Solvent extract by GC, GCMS

Optical methods (Ro)

Gas chemical and isotopic compositions
Gas Samples for Shale Gas Studies

- Canister desorption gas
- Mud gas in drilling
- Producing gas in shale gas wells
- Released gas in gas-tight rock crushing
  - Proposed idea and its significance
  - Preliminary gas chemical compositional results from gas-tight rock crushing
  - Potential application
**Released Gas in Rock Crushing**

- There is a possibility of the presence of isolated pores filled with gases.

- Preserved gas will be released in rock crushing to powder.

- A gas-tight rock crushing cell is critical to test the technique.

- The stainless steel cell from our existing SPEX 8000M Mixer/Mill machine is modified with on-line filter and on/off valve.
Gas-tight Vial for Rock Crushing
Experimental setup for gas-tight rock crushing

- Shale Sample
- Exit port with valve
- Hard Steel Vessel
- Ball Bearing
- 2 inches
Rock Crushing Process and Gas Recovery

Create vacuum;
then seal container
After Crushing, Gas Samples Withdrawn

Gases to chromatograph
Both thermal maturity and gas desorption contribute to changes in CH$_4$/CO$_2$ ratio of released gas from rock crushing.

CH$_4$/CO$_2$ ratios are lower at low thermal maturities because less CH$_4$-rich gas is generated at low maturity levels.

CH$_4$/CO$_2$ ratios decrease with longer rock crushing time because of increasing CO$_2$-rich adsorbed gas contribution.
Similar $\text{CH}_4/\text{CO}_2$ Ratio Changes are Observed in Barnett Shale Samples

- Similar changes in $\text{CH}_4/\text{CO}_2$ ratios are seen in Barnett Shales of various thermal maturity in rock crushing.

- $\text{CH}_4/\text{CO}_2$ ratio changes may indicate free gas preservation.
Proposed Mechanism of Gas Releasing in Shales

- CH$_4$ dominates free gas in the very early stages of rock crushing.
- CO$_2$-rich adsorbed gas is dominant in late stages.
No Obvious Compositional Fractionation Occurs Between $C_1$ and $C_2$ in Rock Crushing

Barnett Shale

Eagle Ford
No Obvious Compositional Fractionation Occurs Between $C_2$ and $C_3$ in Rock Crushing

Barnett Shale

Eagle Ford

![Graphs showing $C_2/C_3$ ratio against crushing time for Barnett Shale and Eagle Ford with different Ro values: Ro=0.58%, Ro=0.8%, Ro=1.0%, Ro=1.2%, Ro=1.4%, Ro=1.6%, Ro=1.7%, Ro=1.9%, Ro=2.0% for Barnett Shale; Ro=0.5%, Ro=0.9%, Ro=1.7%, Ro=2.4% for Eagle Ford.](image)
\( iC_4/nC_4 \) at \( Ro \leq 1.7\% \)

**Barnett Shale**

**Eagle Ford**
$iC_4/nC_4$ at $Ro > 1.7\%$

**Barnett Shale**

- 7112 ft ($Ro=1.96\%$)
- 7192 ft ($Ro=2.01\%$)
- 7223 ft ($Ro=2.07\%$)

**Eagle Ford**

- Blakely #1: $Ro=2.4\%$
- $Ro=2.7\%$
Relationship Between Thermal Maturity and $C_1/C_2$ ratio

![Graph showing the relationship between thermal maturity (Ro) and $C_1/C_2$ ratio for Barnett Shale and Eagle Ford.](image)

- **Barnett Shale** represented by orange circles.
- **Eagle Ford** represented by magenta triangles.
Relationship Between Thermal Maturity and $iC_4/nC_4$ ratio

- Barnett Shale
- Eagle Ford

- kerogen primary cracking gas
- oil secondary cracking gas
- clay mineral catalysis?
Comparison of Gas Chemistry from Rock Crushing Gas and Production Gas

• Gas chemistry data from rock crushing are comparable to those of producing gas in Barnett shale.

• With increasing thermal maturity, iC4/nC4 ratio increases first due kerogen cracking to gas, then decreases after oil starts cracking to gas.
Conclusions

• Liquid hydrocarbons characterization in mudstone can provide information about thermal maturation, organic type and depositional environments.

• CH$_4$/CO$_2$ ratios from core crushing are controlled by both thermal maturity and gas desorption.

• C$_1$/C$_2$ and C$_2$/C$_3$ are good indicators of thermal maturation of organic-rich shales.

• The role of clay mineral catalysis in oil cracking to gas needs to be investigated.

• Quantified released gas amount in rock crushing and gas isotope compositional measurement need to be addressed.
Acknowledgements

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