For more than 20 years petroleum and natural gas exploration, Chinese geologists have discovered two family groups of natural gas in the Tarim basin, China. The first is Coal-type gas: derived from Jurassic coal measures of type-III kerogen, $\delta^{13}C_2 > -28\%$; the second is Oil-type gas: derived from Ordovician, Cambrian marine sources of type-II and type-I kerogens; or oil secondary cracking. $\delta^{13}C_2 < -28\%$.

Gas filling history is an important issue for natural gas exploration, and quantitative gas generation model is an useful tool to address the following issues:

- Gas generation and expulsion from sources
- Gas thermal maturity
- Gas filling history and gas charging time
- Gas reserves evaluation
Three Sets of Potential Source Rocks in the Tarim Basin, China

- Triassic-Jurassic continental source rocks
  - Type III kerogen (humic) with an average TOC of 1.8% to 67%.
- Carboniferous-Permian source rocks
  - Type II and III kerogen with TOC = 0.47% - 5%.
- Sinian-Ordovician marine source rocks
  - Type I kerogen (sapropelite) with TOC = 0.2-3.4%.

Modified from Chen et al., 2000
Tectonic Elements and Gas Fields in the Tarim Basin, China
Structure Cross Section of the Tarim Basin

- **Sinian-Lower Paleozoic Unit**: Highly-mature to post-mature marine carbonate sediments with thickness >9500m
- **Upper Paleozoic Unit**: Mature to highly mature clastic deposits with a maximum thickness of 4500m
- **Mesozoic-Cenozoic Unit**: Terrestrial clastic deposits up to thickness of 11,000m in the sedimentary center.

According to Chen et al., 2000
Carbon Isotopic Compositions are Effective Indicators for Gas Origin Identification

- Coal-type gas possesses heavier carbon isotopes of ethane and propane compared with oil-type gas.
- A positive relationship of $\delta^{13}C_2$ and $\delta^{13}C_1$ and $\delta^{13}C_3$ suggests that the thermal genetic gases from organic matter cracking under high temperature and pressure are a dominant source in the Tarim basin.
- GOR-isotope quantitative model can apply to the understanding of natural gas formation and gas filling history.
Possible Scenario of Gas Generation and Modeling
Flow Chart for Gas Generation
Kinetics Investigation

- Immature source
- Gas yields and carbon isotopes measurement
- Extrapolation
- Ea: activation energy
- Af: frequency factor
- Timing of gas generation, migration and accumulation
Geochemical Properties of Jurassic Coal Selected for Simulation

<table>
<thead>
<tr>
<th>Sample</th>
<th>Geochemistry</th>
<th>HI</th>
<th>Fusinite</th>
<th>Semi-fusinite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coal 1</td>
<td>37.8</td>
<td>70.4</td>
<td>68.3</td>
<td>74.5</td>
</tr>
<tr>
<td>Sample 2</td>
<td>38.4</td>
<td>69.9</td>
<td>68.3</td>
<td>73.6</td>
</tr>
<tr>
<td>Sample 3</td>
<td>37.8</td>
<td>70.4</td>
<td>68.3</td>
<td>74.5</td>
</tr>
<tr>
<td>Sample 4</td>
<td>38.4</td>
<td>69.9</td>
<td>68.3</td>
<td>73.6</td>
</tr>
</tbody>
</table>

‰ δ13C

(mgHC/gTOC)
Gas Generation From Coal Anhydrous Pyrolysis at Two Different Heating Rates

Temperature (°C)

C1 yield (mg/g TOC)

Expt. 20°C/hr

Calcu. 20°C/hr

Expt. 2°C/hr

Calcu. 2°C/hr

C2 yield (mg/g TOC)

C3 yield (mg/g TOC)

Gas Yield (mg/g TOC)
Activation Energy Distribution of Gas Generation From Jurassic Coal

- Frequency factor \( Af = 1E+14 \)
- Average of activation energy:
  - \( C_1 = 58 \text{kcal/mol} \)
  - \( C_2 = 57 \text{kcal/mol} \)
  - \( C_3 = 54 \text{kcal/mol} \)
Carbon Isotopes of Gases From Coal Anhydrous Pyrolysis at Two Different Heating Rates

$\delta^{13}C$ (‰, PDB)

Temperature (°C)

-37
-36
-35
-34
-33
-32
-31
-30

350 375 400 425 450 475 500

$\delta^{13}C_1$ (‰, PDB)

Expt. 20°C/hr

Calcu. 20°C/hr

Expt. 2°C/hr

Calcu. 2°C/hr

$\delta^{13}C_2$ (‰, PDB)

$\delta^{13}C_3$ (‰, PDB)
Laboratory pyrolysis data cannot be directly compared with geological data. Only through extrapolation of kinetic gas isotope fractionation can one use pyrolysis data to predict gas isotope changes with time and temperature.

### Observed Gas Isotope Fractionations in the Laboratory and Nature

<table>
<thead>
<tr>
<th>δ(^{13}\text{C}) Geology</th>
<th>δ(^{13}\text{C}) Laboratory</th>
</tr>
</thead>
<tbody>
<tr>
<td>Smaller Fractionation</td>
<td>Larger Fractionation</td>
</tr>
</tbody>
</table>

**Temperature**

- Laboratory Temperatures
- Geological Temperatures

Laboratory pyrolysis data cannot be directly compared with geological data. Only through extrapolation of kinetic gas isotope fractionation can one use pyrolysis data to predict gas isotope changes with time and temperature.
Extrapolation of kinetic gas isotope fractionation obtained from pyrolysis data is able to predict gas isotope changes with time and temperature under geological condition.

### Kinetics Parameters of Isotope Fractionations For Basin Modeling

<table>
<thead>
<tr>
<th>Process</th>
<th>$\delta_{13C}$</th>
<th>$\sigma$</th>
<th>$E_o$ (kcal/mol)</th>
<th>$\Delta E_H$ (cal/mol)</th>
<th>$\Delta E_L$ (cal/mol)</th>
<th>$\alpha(1)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biomass</td>
<td>-21.2</td>
<td>59.4</td>
<td>80</td>
<td>101</td>
<td>101</td>
<td>1.0</td>
</tr>
<tr>
<td>Basalt carbonate</td>
<td>-23.0</td>
<td>61.6</td>
<td>80</td>
<td>101</td>
<td>101</td>
<td>1.0</td>
</tr>
<tr>
<td>Amorphous carbon</td>
<td>-30.1</td>
<td>61.4</td>
<td>85</td>
<td>102</td>
<td>102</td>
<td>1.0</td>
</tr>
<tr>
<td>Residual asphalt</td>
<td>-25.8</td>
<td>61.6</td>
<td>80</td>
<td>101</td>
<td>101</td>
<td>1.0</td>
</tr>
<tr>
<td>Spent in fuel</td>
<td>-28.0</td>
<td>61.6</td>
<td>80</td>
<td>101</td>
<td>101</td>
<td>1.0</td>
</tr>
</tbody>
</table>

### Summary

- $\delta_{13C}$: Carbon isotope ratio
- $\sigma$: Standard deviation
- $E_o$: Activation energy
- $\Delta E_H$ and $\Delta E_L$: High and Low energy barriers
- $\alpha(1)$: Temperature coefficient

Note: The parameters are for basin modeling and can vary with specific geological conditions and processes.
Geological Application of GOR-isotope Model in Tarim Basin

- Timing of Gas Excretion and Expulsion
- Gas filling history
- Gas thermal maturity
- Gas reserves estimation
- Gas recharging time
Burial Thermal History of Jurassic Source Rock in the Tariq Basin

According to Liang et al. 2003
Gas Generation from Jurassic Coal Source in the Tarim basin

Cumulative gas (scf/ton TOC)

Gas produced from the Jurassic coal expelled at 27mybp (or Ro ~ 0.95%)
Modeling Carbon Isotopes of Expelled Gases from Jurassic Coal: Match with Geological Observation of Natural Gases in Reservoirs.

\[ \delta^{13}C_1, \delta^{13}C_2, \delta^{13}C_3(\text{‰}) \]

Carbon isotope model of expelled gases from Jurassic coal.
Thermal Maturity of Coal-type Gas in Tarim Basin

[Graph showing data points and axes labeled with δ13C-ethane and C1/(C2+C3)]

- Significant contribution from secondary cracking
- Primary gas from kerogen cracking
Distribution of Gas Fields in Kuqa Depression

Ro (%) contour of Jurassic coal gas source in Kuqa Depression (according to Qin et al., 2006)
Gas Reserves Prediction By Gas Geochemistry Isotope Model

- Geological gas reserve (10^8 m^3)
- Gas yield (scf/ton TOC)
- Expelled gas amount from the Jurassic coal

Diagram showing the relationship between δ13C values and gas reserves.
Kula 2 Large-size Gas Field Was Probably Charged About 2 mybp.
Conclusions

- Oil-type gas and coal-type gas can be clearly differentiated by the carbon isotopic compositions of C1, C2, and C3 in natural gases from the Tarim basin. Oil-type gas possesses a lighter carbon isotope of ethane and propane compared with that of coal-type gas.

- Thermal genetic gases from organic matter cracking under high temperature and pressure are a dominant source in the Tarim basin.

- Quantitative kinetics model provides a useful tool for dynamically understanding gas recharging history, determining gas maturity, predicting gas reserves and recharging time in an effective trap.

- Expelled gas from Jurassic coal occurred about 27 my before present time once the produced gas is abundant enough to meet coal absorption.

- The recharging of Kela 2 large-sized gas field probably occurred about 2 my before present time.

- Expelled gas retained in the Jurassic coal until faults as gas migration pathway became available at about 2 my before present time.