

# Kinetics and Mechanism of Shale Gas Formation: A Quantitative Interpretation of Gas Isotope “Rollover” for Shale Gas Formation

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## Summary

The production and geochemical data show that the potential and characteristics of hydrocarbon generated and remaining in shales at high maturity are different from the prediction using the methods for conventional gas reservoirs, rendering the difficulties in resource assessment. Quantitative studies of carbon isotope composition of methane, ethane, propane and CO<sub>2</sub> in shale gas and other high maturity gas reservoirs, along with isotope kinetic fractionation, indicate that water-reforming of high-mature organic matter and the consequent Fischer-Tropsch process is a highly possible mechanism for shale gas generation. This mechanism is also consistent with the isotope phenomenon (isotope reversal) and stabilized gas production from the producing field.

## 1. Introduction

Recently abundant production and geochemical data of shale gas accumulated during the extensive exploration and development in the U.S. A series of measurements on several shale reservoirs discovered “rollover” of ethane carbon isotope composition ( $\delta^{13}\text{C}_2$ ), iso-butane/n-butane ratio ( $i\text{C}_4/n\text{C}_4$ ), and CO<sub>2</sub> carbon isotope composition ( $\delta^{13}\text{C}_{\text{CO}_2}$ ) in shale gas; that is, the trend of above parameters with maturity reverses at higher maturity. This special phenomenon indicates an unconventional generation mechanism of shale gas.

Meanwhile, the above “reversal” trend is common in higher production wells instead of the lower ones. The correlation between shale gas productivity and natural gas geochemistry suggests that hydrocarbon generation potential, rather than physical properties of shale rock, remains the key factor controlling the resource of shale gas.

An accurate assessment on shale gas resource needs a better understanding of the mechanism of hydrocarbon generation in shale gas. Shale gas is formed under special conditions: 1) it is the gas that remains in source rock; 2) it is generated from organic matter at high maturity.

## 2. Mechanistic studies of shale gas generation

The unique geochemical characteristics of shale gas can be attributed to one or more processes of shale gas generation:

### 1) Kerogen Cracking

From both laboratory pyrolysis and nature field samples, it is generally understood that when maturity increases, gas wetness ( $\text{C}_{2+}\%$ ) decreases and carbon isotope ( $\delta^{13}\text{C}$ ) of methane, ethane and propane increase.

### 2) Cracking of different components of hydrocarbon

Gas products from oil and condensate cracking have higher wetness and lighter  $\delta^{13}\text{C}$ . But if components in gas start to crack, the gas becomes drier and the  $\delta^{13}\text{C}$  value of these components becomes heavier. In the shale gas sample with “reversal” phenomenon, even though the gas is dry (wetness < 5%), the values of  $\delta^{13}\text{C}_2$  and  $\delta^{13}\text{C}_3$  become dramatically light with decreasing wetness. This indicates that ethane and propane are cracking products rather than reactants.

Meanwhile, the reversal of the  $iC_4/nC_4$  value at low wetness may indicate faster cracking rates of isobutane. This is consistent to the activation energy difference of these molecules (Figure 1).

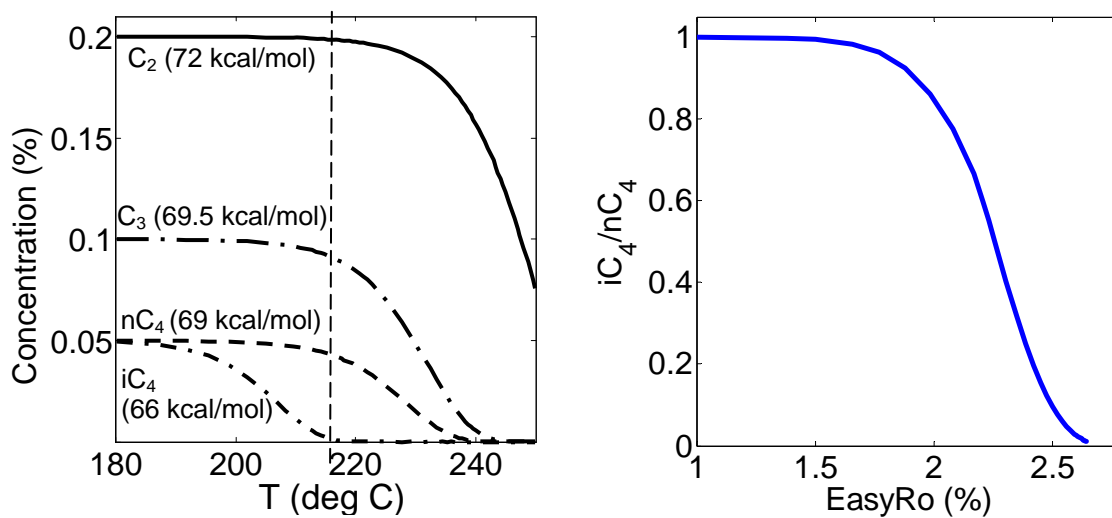


Figure 1: Simulation of  $C_{2-4}$  hydrocarbon concentration and  $iC_4/nC_4$  ratio with increasing maturity of shale gas.

### 3) Fractionation related to expulsion

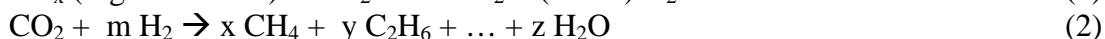
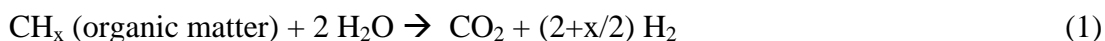
Migration may cause fractionation between hydrocarbons with different molecular size and shape, but little isotopic fractionation.

### 4) Combination or product mixing of several of the above processes

Theoretically, the “rollover” of  $\delta^{13}C_2$  can be obtained by mixing “ideal” amount of primary gas at different a stage and secondary gas. The contribution by this mechanism can not be ruled out, but it needs a strict ratio of its end members. It is hard to explain the broad existence of “rollover” in many shale gas basins, in particular the light  $CO_2$  carbon isotope after the “rollover”.

### 5) Other special processes in shale gas generation

The “rollover” of  $CO_2$  carbon isotope composition in shale gas suggests water reforming (1) and Fischer-Tropsch like reaction (2), which are common reactions in chemical industry:



Reaction 1 brings about a light carbon isotope composition of  $CO_2$ . Considering that Reaction 2 is much faster than Reaction 1—that is, Reaction 1 is the rate-limiting step—the overall Reactions of 1 and 2 will also generate light  $CO_2$ . The conventional Fischer-Tropsch product has much higher carbon numbers and the most commercial processes are using cobalt or iron catalyst. It is unlikely one will find metallic compounds in the subsurface, but the iron (II) oxide is very possible under reducing environment of subsurface hydrocarbon reservoir. Under geological condition, it is possible that the reaction between  $CO_2$  and hydrogen produces methane with little ethane and propane<sup>1</sup>. Thus Reaction 2 may generate light hydrocarbon compounds with

<sup>1</sup> F.-W. Ji, H.-Y. Zhou, Q.-H. Yang (2007), Abiotic synthesis of butane and pentane from  $CO_2$  and  $H_2$  under hydrothermal conditions. *Geochimica*, 36(2) 171-175.

extremely high dryness. These product properties are consistent with the shale gas geochemical composition. Moreover, if this mechanism occurred during shale gas formation, it will, to a large extent, affect the hydrocarbon generation potential and gas resources in shales. Therefore, in this work, our research focuses on the possibility of above mechanisms.

### 3. Thermodynamics and kinetics of organic matter reforming

We applied iso-octane (2,2,4-trimethyl-pentane) as a model molecule for hydrocarbon reforming. Thermodynamic calculation indicates that iso-octane reforming is favorable at higher temperature, CO<sub>2</sub> methanization is favorable at lower temperature, and the overall reaction of iso-octane disproportionate to methane and CO<sub>2</sub> is thermodynamically favorable at all temperature ranges.

As a competing process, water-reforming of hydrocarbon has a lower activation energy (about 66 kcal/mol) and lower frequency factor (about 10<sup>14</sup> s<sup>-1</sup>) than cracking. At geological temperature (< 250 °C) water reforming is more favorable, while at laboratory temperature (> 400 °C) cracking is more favorable. This makes chemical simulation of hydrocarbon reforming rather difficult, because the cracking products will be dominant. However, our preliminary results still show that the hydrocarbon yield increased dramatically in the presence of water during the hydrolysis of iso-octane (Figure 2). This indicates that water is involved in the reaction.

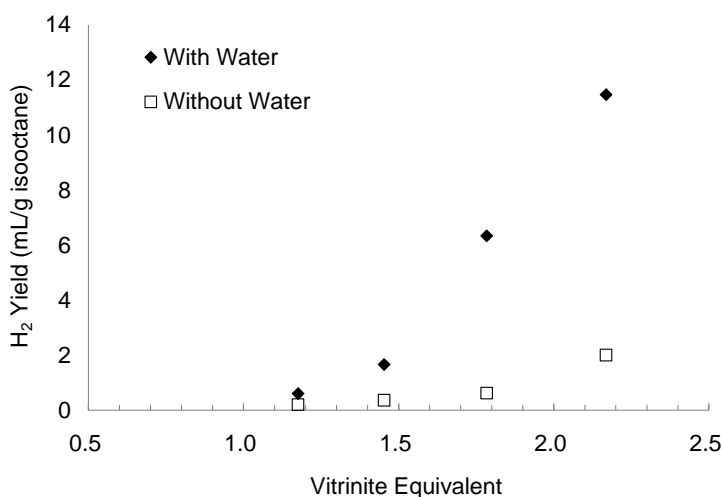


Figure 2: Hydrogen yield from iso-octane hydrolysis in the presence/absence of water.

### 4. Organic matter reforming as natural gas generation mechanism in conventional reservoirs

The proposed mechanism of hydrocarbon reforming and consequent Fischer-Tropsch reaction is characteristic of light carbon  $\delta^{13}\text{C}_{\text{CO}_2}$  (< 10 per mil, indicating organic origin) and  $\delta^{13}\text{C}_2 > \delta^{13}\text{C}_1$ . It occurred at higher maturity, and the in-source shale reservoir has the beneficial condition to preserve this type of gas without being diluted by earlier-generated gas. Under suitable conditions, these mechanism and corresponding geochemical features also occur in some conventional gas reservoirs. Table 1 lists the carbon isotope composition of CO<sub>2</sub> and hydrocarbon of some natural gas samples. Previous researchers attributed the reversed series of  $\delta^{13}\text{C}_3 > \delta^{13}\text{C}_2 > \delta^{13}\text{C}_1$  to abiogenic origin. However, light  $\delta^{13}\text{C}_{\text{CO}_2}$  coexists in the hydrocarbon reservoirs with the reversal phenomenon, and the CO<sub>2</sub> reservoirs have heavier  $\delta^{13}\text{C}_{\text{CO}_2}$  and extremely low hydrocarbon concentration. This indicates that hydrocarbons with reversed  $\delta^{13}\text{C}$  have a similar source with organically originated CO<sub>2</sub>, and the

mechanism of reforming and Fischer-Tropsh reaction during magma intrusion in these areas reasonably explains the formation of these gases.

*Table 1: Carbon isotope composition of hydrocarbon and CO<sub>2</sub> in the Songliao Basin, China*

Sample No.	$\delta^{13}\text{C}_1$	$\delta^{13}\text{C}_2$	$\delta^{13}\text{C}_3$	$\delta^{13}\text{C}_{\text{CO}_2}$
1	-28.3	-33.2	-34.3	-13
2	-26.9	-33.8	-34.2	-8.2
3	-27.5	-29.3	-31.4	
4	-27.9	-31.1	-32.8	-15.9
5	-25.9	-32.4	-33.1	-11.1
6	-28.3	-31.1	-33.5	-14.8
7	-27	-30.4	-32.3	-12.3

## 5. Conclusions

Carbon isotope composition of hydrocarbons and CO<sub>2</sub> in shale gas and other high-maturity gas reservoirs indicate that water-reforming and the consequent Fischer-Tropsch-like process make up a possible mechanism for natural gas generation at high maturity. This mechanism is consistent with thermodynamic and kinetic condition in the corresponding geological background and explains the isotope phenomenon (isotope reversal) and gas well production of shale gas.