

## Kinetic Parameters of Methane Generated from Source Rocks in the Kuqa Depression of Tarim Basin and Their Application

LI Xianqing<sup>1,2,\*</sup>, XIAO Xianming<sup>1</sup>, MI Jingkui<sup>1</sup>, TANG Yongchun<sup>3</sup>, XIAO Zhongyao<sup>4</sup>,  
LIU Dehan<sup>1</sup>, SHEN Jiagui<sup>1</sup>, YANG Yunfeng<sup>2</sup>, WANG Yan<sup>2</sup> and DONG Peng<sup>2</sup>

1 *State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry,  
Chinese Academy of Sciences, Guangzhou 510640, China*

2 *State Key Laboratory of Coal Resources and Safe Mining, China University of Mining and  
Technology, Beijing 100083, China*

3 *Research Center of Petroleum Energy and Environment, California Institute of Technology,  
21910 Currier Rd, Walnut, CA 61769, USA*

4 *Research Institute of Exploration and Development, Tarim Oil Field Company, PetroChina,  
Korla, Xinjiang 841000, China*

**Abstract:** In a thermal simulation experiment of gold tubes of closed-system, calculating with the KINETICS and GOR-ISOTOPE KINETICS software, kinetic parameters of gas generation and methane carbon isotopic fractionation from Triassic–Jurassic hydrocarbon source rocks in the Kuqa depression of Tarim Basin are obtained. The activation energies of methane generated from Jurassic coal, Jurassic mudstone and Triassic mudstone in the Kuqa Depression are 197–268 kJ/mol, 180–260 kJ/mol and 214–289 kJ/mol, respectively, and their frequency factors are  $5.265 \times 10^{13} \text{ s}^{-1}$ ,  $9.761 \times 10^{11} \text{ s}^{-1}$  and  $2.270 \times 10^{14} \text{ s}^{-1}$ . This reflects their differences of hydrocarbon generation behaviors. The kinetic parameters of methane carbon isotopic fractionation are also different in Jurassic coal, Jurassic mudstone and Triassic mudstone, whose average activation energies are 228 kJ/mol, 205 kJ/mol and 231 kJ/mol, respectively. Combined with the geological background, the origin of natural gas in the Yinan-2 gas pool is discussed, and an accumulation model of natural gas is thus established. The Yinan-2 gas is primarily derived from Jurassic coal-bearing source rocks in the Yangxia Sag. Main gas accumulation time is 5–0 Ma and the corresponding Ro is in the range from 1.25%–1.95%. The loss rate of natural gas is 25%–30%.

**Key words:** hydrocarbon source rock, methane generation, carbon isotopic fractionation, kinetics, Kuqa Depression, Tarim Basin

### 1 Introduction

The kinetic study of gas generation and methane carbon isotopic fractionation from hydrocarbon source rocks is one of the important progresses of petroleum and natural gas geochemistry in recent years (Behar et al., 1997; Lorant et al., 1998; Tang et al., 2000; Cramer et al., 1998, 2001; Liu et al., 1998, 2002; Xiong et al., 2002; Gao et al., 2003; Li et al., 2003a, 2003b, 2004, 2005, 2006). Combined with the burial history and heating history of the basin, the kinetic modeling of gas yield and methane carbon isotopic fractionation can reproduce the process of gas generation and accumulation on the basis of the data of thermal

simulation experiment on hydrocarbon source rocks. It provides a new way for the dynamic evaluation and prediction of natural gas (Tang et al., 2000; Cramer et al., 1998, 2001; Li et al., 2003a, 2004, 2005, 2006).

Many researches (Behar et al., 1997; Boreham et al., 1999; Tang et al., 2000; Cramer et al., 1998, 2001) have proved that hydrocarbon source rocks of different types and different maturities may have different kinetic parameters of gas generation and carbon isotopic fractionation, and sometimes the difference is great. Even if organic matter of the same type in a basin with different sediments and evolutionary histories, there are obvious differences in the kinetic parameters of gas generation and methane carbon isotopic fractionation. So, it is necessary to study the kinetic parameters of gas generation and carbon isotopic

\* Corresponding author. E-mail: lixq@gig.ac.cn

**Table 1 Basic geochemical data of source rock samples in the Kuqa Depression**

Sample No.	Depth (m)	Age	Lithology	Ro (%)	TOC (%)	Tmax (°C)	S <sub>1</sub> (mg/g)	S <sub>2</sub> (mg/g)	HI (mg/g)
yn2-4	4316.8	J <sub>2k</sub>	coal	0.88	76.53	448	6.34	112.80	147.39
yn2-6	4400.4	J <sub>1y</sub>	mudstone	0.89	3.53	442	0.38	3.74	105.65
yn2-9	5000.3	T <sub>3t</sub>	mudstone	1.05	1.12	473	0.07	0.52	46.43

fractionation in a specific sedimentary basin.

Although many scholars (Qin, 1999; Wang et al., 1999; Jia et al., 2000, 2001; Li et al., 2001; Liang et al., 2002, 2003; Zhao and Dai, 2002; Zhao et al., 2002; Zhou et al., 2001; Song et al., 2002; Wang et al., 2002; Mei et al., 2004) have done a lot of geological and geochemical researches, the quantitative experimental study of gas generation kinetics in the Kuqa Depression of Tarim Basin is still not enough. The research and application of the kinetic parameters of gas generation and methane carbon isotopic fractionation from the Triassic-Jurassic source rocks in this region have not been reported. Based on the results of the thermal simulation experiment of gold tube-high pressure vessels of closed-system, and using KINETICS and GOR-ISOTOPE KINETICS software, the kinetic parameters of gas generation and methane carbon isotopic fractionation from different source rocks in the Kuqa Depression of Tarim Basin are obtained. Combined with the burial history and thermal history of the Kuqa Depression, the calculation of the kinetic modeling in the geological condition is carried out with the kinetic parameters above. Thus, the origin and formation model of natural gas from the Yinan-2 gas pool is studied further.

## 2 Samples and Experimental Methods

### 2.1 Samples

The Kuqa Depression is a compounded foreland basin, which is formed in the Middle Cenozoic Era and basically consists of terrestrial deposits. It has experienced three main evolutionary stages, i.e., the Late Permian to Triassic foreland basin, the Jurassic intra-continental depression basin and the Cretaceous to Quaternary re-constructed foreland basin stages (Jia, 1997; Wei et al., 2000; Jia et al., 2001). It also experienced complicated geological evolutionary history and deep burial process, especially in the Himalayan Epoch. In the Mesozoic strata, Triassic-Jurassic source rocks were deeply buried and evolved quickly, and then got matured up to high-over mature stages in a short period (Liang et al., 2002; Jia et al., 2000). In the sedimentary center of the Kuqa Depression (i.e., the Baicheng Sag), the vitrinite reflectance (Ro) of the source rocks can be more than 2.5%. Even in the edge of the basin, where buried shallow, Ro has already been up to 0.8% (Wang et al., 1999; Liang et al., 2002, 2003). So, it is difficult to find low mature source rocks, with Ro value of less than 0.6% for pyrolysis experiment. However, this

does not have great influence on gas generation, because gaseous hydrocarbon mainly generated at the medium-high mature stages (Ro>1.0 %).

The studied samples, including a Jurassic coal, a Jurassic mudstone and a Triassic mudstone, are selected from Well Yinan-2 in the Kuqa Depression of Tarim Basin. Basic geochemical characteristics of these source rock samples are listed in Table 1. For the Jurassic coal-bearing source rocks from Kezilenuer Formation and Yangxia Formation, they have type III organic matter, and their Ro values are 0.88% and 0.89%, respectively. The Triassic mudstone also contains type III organic matter, but it has higher maturity (Ro value up to 1.05%). These samples are ground into 100 meshes, extracted by MBA solvents (methanol: acetone: benzene = 1: 2.5: 2.5) and remove minerals, and then prepare kerogens.

### 2.2 Experimental methods

The closed-system of gold tube-high pressure reaction vessels is chosen for pyrolysis experiments (Liu et al., 1998; Tang et al., 2000; Li, 2004). The heating temperatures range from 300 °C to 600 °C. The pyrolysis pressure is kept at 50 MPa. The heating rates are 20 °C/h and 2 °C/h. After the pyrolysis experiment, the GC and GC-IRMS analyses are needed for the pyrolysis gas in the gold tubes.

The pyrolysis gas is collected using a vacuum pump. Then, a gas composition analysis is performed on an HP5890 II gas chromatography and quantified by an internal standard method. The GC condition: a Poraplot Quadax column (30 m×0.25 mm×0.25 μm) is used. Helium is used as the carrier gas. The temperature program used is isothermal for 2 min at 50 °C, programmed at 4 °C/min to 180 °C, and then holds at 180 °C for 15 min.

The carbon isotope ratio analysis is performed on a VG Isochrom II gas chromatograph-mass spectrometer. The error of the results of carbon isotope is less than ±0.3‰ (PDB). The GC was equipped with a Poraplot Quadax column (30 m×0.32 mm×0.25 μm). Helium is used as the carrier gas. The temperature program used is isothermal for 3 min at 50 °C, programmed at 4 °C/min to 150 °C, and then holds at 150 °C for 8 min.

## 3 The Yield Characteristics of Methane Generated from Source Rocks and the Calculation of Kinetic Parameters

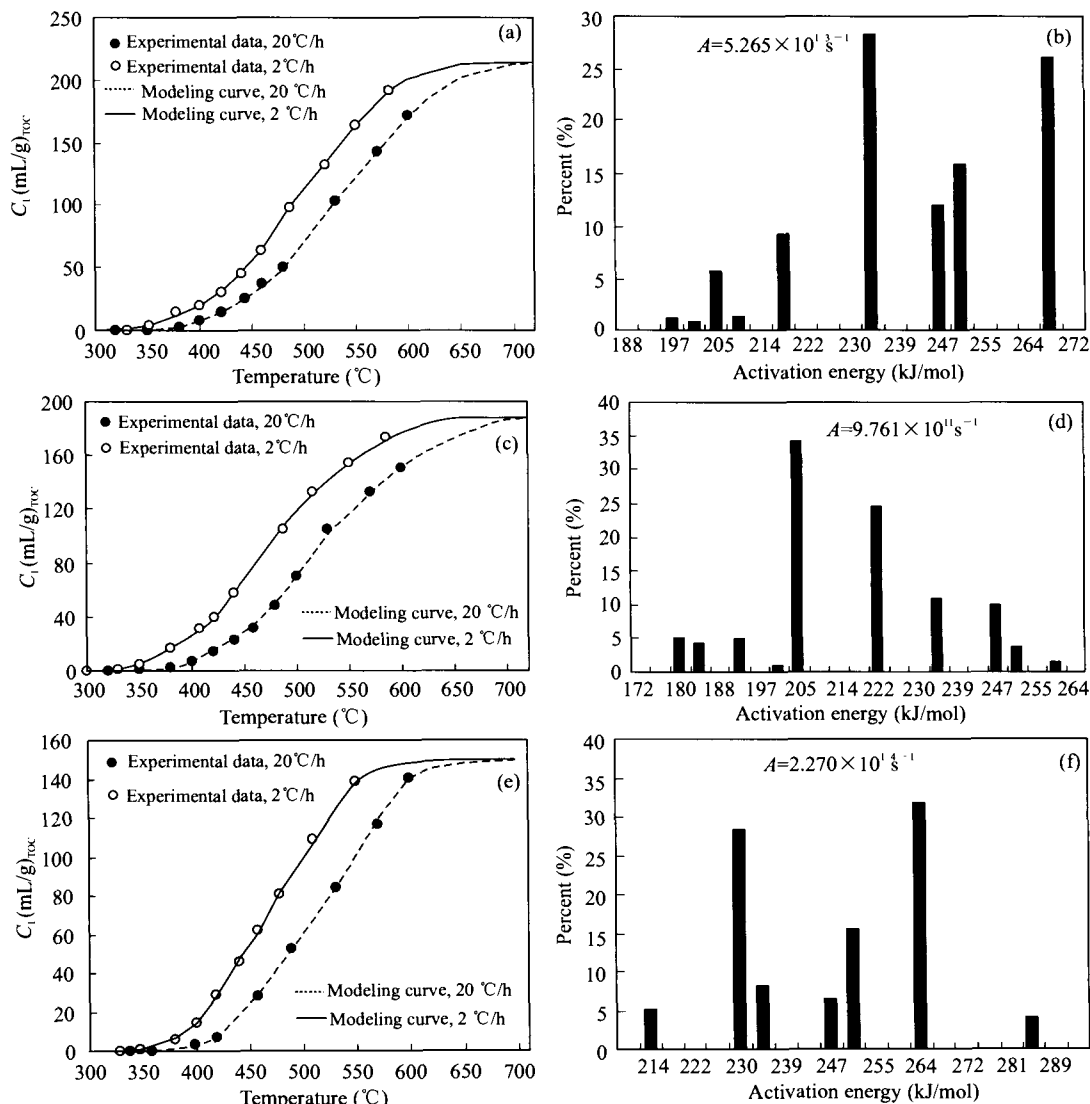


Fig. 1. Methane yields and their kinetic calculations from source rocks in the Kuqa Depression. (a), (c), (e) showing the methane yields generated from Jurassic coal, Jurassic mudstone and Triassic mudstone, respectively; (b), (d), (f) showing the activation energy distributions of methane generated from Jurassic coal, Jurassic mudstone and Triassic mudstone, respectively.

### 3.1 The yield characteristics of methane generated from source rocks

The pyrolysis experimental results at two different heating rates (20 °C/h and 2 °C/h) of methane generated from the Triassic-Jurassic source rocks in the Kuqa depression of Tarim Basin are shown in Fig. 1a, c and e. The yields of methane are closely related to the pyrolysis temperatures and the heating rates. The yields of methane increase with increasing the pyrolysis temperatures. The rise of methane yield at the heating rate of 2 °C/h is more than that at the heating rate of 20 °C/h. The Jurassic coal and Jurassic mudstone generated more methane than the Triassic mudstone, especially at high thermal evolutionary stage. For instance, at heating rate of 20 °C/h, when the pyrolysis temperature reached 600 °C, Jurassic coal,

Jurassic mudstone and Triassic mudstone produced 173 mL/g·TOC, 156 mL/g·TOC and 141 mL/g·TOC cumulative methane, respectively. It is suggested that Jurassic coal-bearing source rocks have higher potential of gas generation than Triassic mudstone.

It should be pointed that there are a few differences between Jurassic coal and Jurassic mudstone, although they are in the same coal-bearing strata. The methane yield of Jurassic coal is slightly higher than that of Jurassic mudstone. It indicates that coal has better gas generation potential than mudstone. The organic petrological results (Li, 2004) show that Jurassic coal in Well Yanan-2 contains predominantly desmocollinite (70%) and significant amount of exinite (7%), while Jurassic mudstone contains less exinite (3%) and higher inertinite (15%).

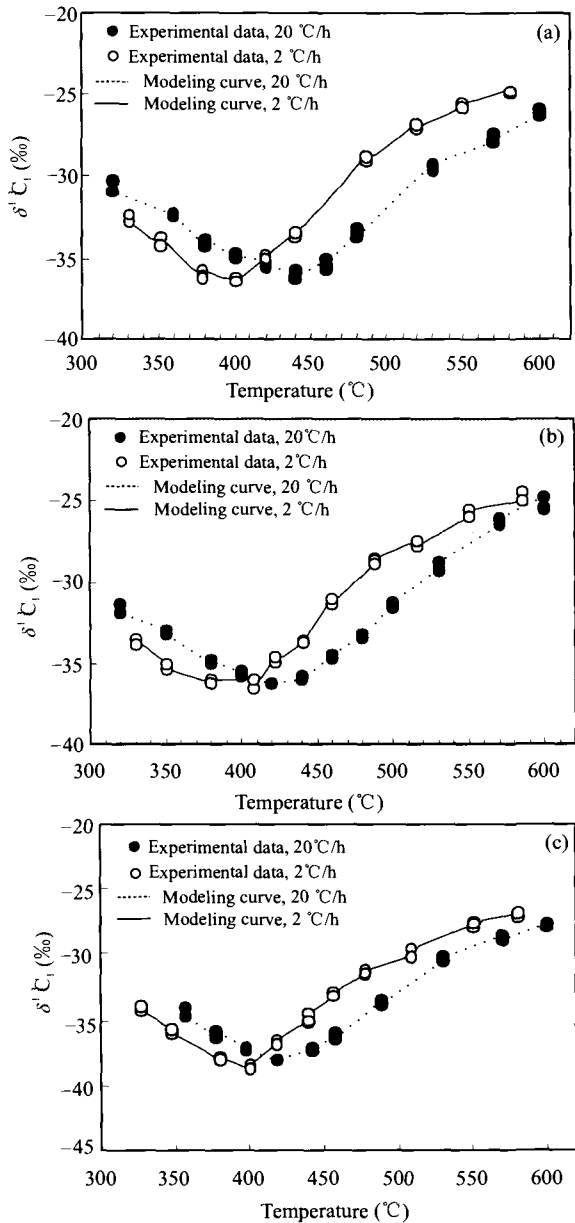


Fig.2. The methane carbon isotope characteristics of source rocks in the Kuqa Depression and their kinetic calculations. (a), (b), (c) showing Jurassic coal, Jurassic mudstone and Triassic mudstone, respectively.

### 3.2 The calculation of kinetic parameters of methane generation

The experimental data processing and the kinetic parameters calculation of methane generation were carried out on the computer with the KINETICS Program developed by the Lawrence Livermore National Laboratory of U.S.A. The calculation method in detail can refer to Liu et al. (1998) and Li (2004). The activation energy distribution and frequency factor can be obtained by the kinetic calculation with the software.

The kinetic parameters of methane generated from

Triassic-Jurassic source rocks in the Kuqa Depression are shown in Fig.1 (b), (d) and (f). The Triassic-Jurassic source rocks of Well Yinan-2 have a wide activation energy distribution in the range of 180–289 kJ/mol. The ranges of activation energy distribution of methane generation in Jurassic coal and Jurassic mudstone are 197–268 kJ/mol and 180–260 kJ/mol. The main peaks of activation energies of methane generation in Jurassic coal and Jurassic mudstone are 234 kJ/mol and 205 kJ/mol. Their frequency factors are  $5.265 \times 10^{13} \text{ s}^{-1}$  and  $9.761 \times 10^{11} \text{ s}^{-1}$ , respectively. Triassic mudstone also has a wide distribution of activation energy in the range of 214–289 kJ/mol. The main peak of activation energy is 264 kJ/mol, and its frequency factor is  $2.270 \times 10^{14} \text{ s}^{-1}$ . All these parameters reflect the differences of methane generation in source rocks with different characteristics, even for the same type III organic matter.

It is known that several mathematical models to calculate the kinetic parameters of gas generation have been developed (Ungerer et al., 1987; Behar et al., 1997; Lu, 1996). Many researches have demonstrated the kinetic model of parallel first-order reaction and it has been widely applied in the world, because it can provide reasonable modeling results by kinetic calculation with pyrolysis experimental data (Lu et al., 2000; Liu et al., 1998, 2002). On the basis of the parallel first-order reaction model, the KINETICS software adopted in this study was developed by the Lawrence Livermore National Laboratory of U.S.A. and used to describe the dynamic process of gas generation from kerogens (Liu et al., 1998, 2002). The modeling curves in Fig.1 (a), (c) and (e) are fitted by the KINETICS software. The experimental data in Fig. 1 (a), (c) and (e) are obtained from the pyrolysis products of gold tube-high pressure vessels of closed-system. Obviously, the kinetic modeling results of the studied samples are coincided with their experimental data [Fig.1 (a), (c) and (e)].

### 3.3 The kinetic parameters calculation of methane carbon isotopic fractionation

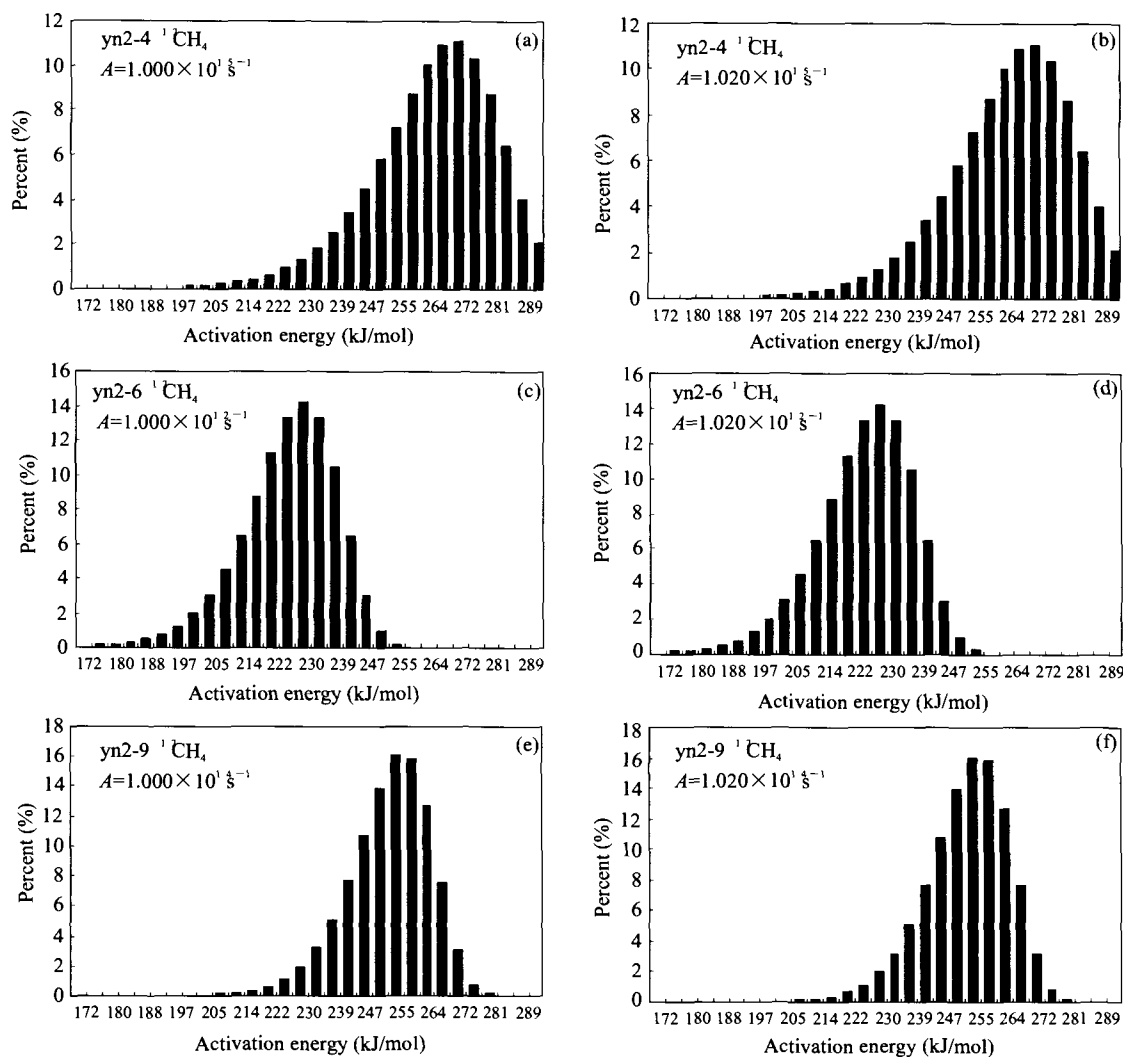
The methane carbon isotope values of Jurassic coal, Jurassic mudstone and Triassic mudstone in the Kuqa Depression of Tarim Basin are measured and shown in Fig. 2. The  $\delta^{13}\text{C}_1$  value of pyrolysis gas from Jurassic source rocks (i.e., coal and mudstone) is between  $-37\text{‰}$ – $-25\text{‰}$ , while that of Triassic mudstone is between  $-39\text{‰}$ – $-27\text{‰}$ . With the pyrolysis temperature increasing, the  $\delta^{13}\text{C}_1$  values of Jurassic coal, Jurassic mudstone and Triassic mudstone have the similar variation trend. Their  $\delta^{13}\text{C}_1$  values decrease at first, and reach the minimum values at the temperature of 400–420 °C, and then gradually increase as the temperature higher than 420 °C.

According to the theoretical kinetic model of methane carbon isotopic fractionation (Tang et al., 2000; Cramer et

**Table 2 the kinetic parameters of methane generated from source rocks in the Kuqa Depression**

Samples	$\alpha$	$\beta_L$ (J/mol)	$\beta_H$ (J/mol)	$E_o$ (kJ/mol)	$\sigma$ (J/mol)	$\gamma$
Jurassic coal	1.020	137.66	522.14	228	32.74	0.01094
Jurassic mudstone	1.020	117.98	247.52	205	22.86	0.01094
Triassic mudstone	1.020	109.19	204.19	231	11.60	0.01090

Abbreviations:  $\alpha$  is the isotopic fractionation factor;  $\beta_L$  and  $\beta_H$  are the lowest and highest values of enthalpy for isotopic fractionation, respectively;  $E_o$  is the average activation energy;  $\sigma$  is the variance;  $\gamma$  is the activation energy threshold.



**Fig.3. the activation energies distributions of  $^{12}\text{C}$ -methane and  $^{13}\text{C}$ -methane generated from source rocks in the Kuqa Depression.**

(a), (c), (e) showing the activation energy distribution of  $^{12}\text{C}$ -methane from Jurassic coal, Jurassic mudstone and Triassic mudstone, respectively; (b), (d), (f) showing the activation energy distribution of  $^{13}\text{C}$ -methane from Jurassic coal, Jurassic mudstone and Triassic mudstone, respectively.

al., 2001; Li et al., 2003b, 2005),  $^{13}\text{CH}_4$  and  $^{12}\text{CH}_4$  are regarded as two different gaseous products, and then their reaction rates and yields are calculated. The variations of  $^{13}\text{CH}_4$  and  $^{12}\text{CH}_4$  are mainly reflected in their different activation energies.

The kinetic parameters of methane carbon isotopic fractionation are calculated with the GOR-ISOTOPE KINETICS software. The method follows the same procedure published by Tang et al. (2000). The kinetic parameters of methane carbon isotopic fractionation from

Jurassic coal, Jurassic mudstone and Triassic mudstone in the Kuqa Depression are shown in Table 2 and Fig. 3. The average activation energies of Jurassic coal, Jurassic mudstone and Triassic mudstone are 228 kJ/mol, 205 kJ/mol and 231 kJ/mol, respectively. Their activation thresholds are 0.01094, 0.01094 and 0.01090. It is demonstrated that the modeling results of methane carbon isotopic fractionation are consistent with the experimental data.

From the knowledge above, we know that although the

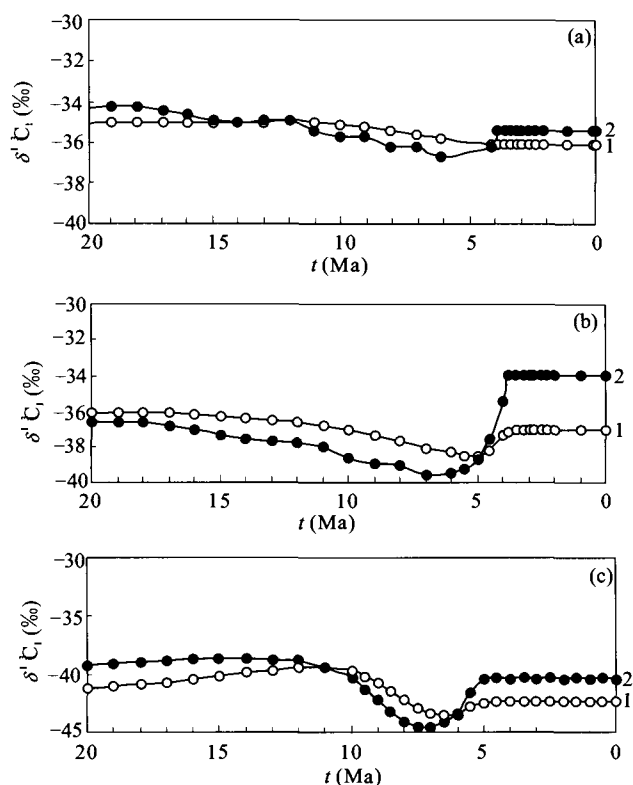


Fig.4. the kinetic calculation results of carbon isotopic fractionation of methane generated from source rocks in Well Yinan 2.

(a), (b), (c) showing Jurassic coal, Jurassic mudstone and Triassic mudstone, respectively. 1 – Instantaneous  $\delta^{13}C_1$ ; 2 – Cumulative  $\delta^{13}C_1$ .

Triassic-Jurassic source rocks in the Kuqa Depression belong to the same type III organic matter, there are still differences in the behavior of gas generation. Therefore, the kinetic parameters of gas generation and methane carbon isotopic fractionation in different source rocks should be obtained. This is essential for the kinetic calculation in the geological condition, and also important for the basin modeling, source rock evaluation, hydrocarbon generation calculation and resources prediction.

#### 4 Application: Origin and Formation Model of Natural Gas from the Yinan-2 Gas Pool

The recent advances (Tang et al., 2000; Cramer et al., 2001; Li et al., 2004, 2005, 2006) show that the kinetics parameters of methane generation and carbon isotopic fractionation have been effectively applied in the formation process of natural gas. Combined with the geological background, the yields and carbon isotope values of methane generated from source rocks can be calculated with their kinetic parameters, and then apply them to the study of the origin and formation process of natural gas. Here, we take the Yinan-2 gas pool in the Kuqa Depression of Tarim Basin as a case study. Based on the previous

researches (Liang et al., 2002; Zhao and Dai, 2002; Zhao et al., 2002; Li et al., 2001; Gao et al., 2002), the origin and formation model of natural gas from Yinan-2 gas pool is further investigated with the kinetic calculation of methane generation and carbon isotopic fractionation.

The Yinan-2 gas pool is located in the south of the Yiqilike anticline, which is the eastern zone of Kelasu-Yiqikelike tectonic belt in Kuqa Depression, Tarim Basin. It is a fault-nose structure, which has a relatively high strata uplift, stronger tectonic deformation and develops a thrust fault (Liang et al., 2002; Gao et al., 2002). The Yinan-2 fault-nose structure and the fault developed relatively early, mainly at the end of Cretaceous Period. However, its structure basically remains unchanged from the end of Cretaceous Period to the Kuqa Formation ( $N_{2k}$ ) of Pliocene. After the deposition of the Kuqa Formation ( $N_{2k}$ ) of Pliocene, especially at the late stage of Himalayan, the present south-inclined tectonic pattern formed at one time with the uplift of the southern Tianshan Mountains and the intense southward extrusion. Therefore, the formation time of Yinan-2 gas pool should be later than the deposition of the Kuqa Formation ( $N_{2k}$ ) of Pliocene (5.3 Ma, Zhao and Dai, 2002).

The Yinan-2 gas pool belongs to an ultra-high pressure gas pool, which has a pressure of 68.59–83.47Mpa and a pressure factor of 1.43–1.87, average about 1.70 (Gao et al., 2002). Natural gas of the Yinan-2 gas pool has relatively lower maturity, which is composed of 88.2%–93.9% of methane and 4.2%–6.6% of heavy hydrocarbon ( $C_2^+$ ). Its dryness coefficient ranges from 90% to 94%, average 92.2%, and its methane carbon isotope ratio is  $-32.2\text{‰}$ . According to the formula of  $\delta^{13}C_1$ -Ro of coal-derived gas by Dai et al. (1989, 1992) and Xu et al. (1994), the calculated Ro values are between 1.0%–1.8%. The Yinan-2 gas originates from Jurassic coal measures source rocks on the basis of the characteristics of  $\delta^{13}C_1$  and  $\delta^{13}C_2$ . It has proposed that natural gas of the Yinan-2 gas pool and other gas pools of the Yiqikelik structure is primarily derived from coal-bearing sequences, on the basis of the carbon isotope characteristics of light hydrocarbons from source rocks pyrolysates (Li et al., 2001).

According to the burial evolutionary history and thermal history obtained from Liang et al. (2000), with the combination of the kinetic parameters of methane generation and carbon isotopic fractionation [Fig. 1b, d, f; Table 2 and Fig. 3], the calculations of kinetic modeling of Jurassic coal and Triassic mudstone from Well Yinan 2 and the center of Yangxia Sag in the Kuqa Depression of Tarim Basin are carried out, which are shown in Figs. 4 and 5.

The kinetic calculation results of carbon isotopic fractionation demonstrate that gas generation time of Middle-Lower Jurassic coal from Well Yinan-2 is relatively

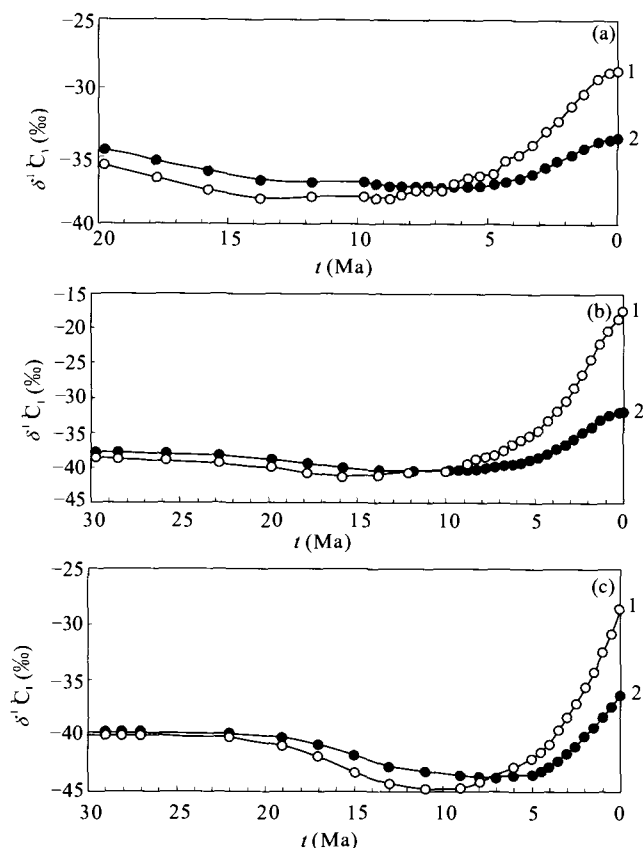


Fig.5. the kinetic calculation results of carbon isotopic fractionation of methane generated from source rocks in the center of Yangxia Sag.

(a), (b), (c) showing Jurassic coal, Jurassic mudstone and Triassic mudstone, respectively. 1 - Instantaneous  $\delta^{13}C_1$ ; 2 - Cumulative  $\delta^{13}C_1$ .

late (Li, 2004). The present methane conversion rate is only 0.13 and the yield of methane is about 25 mL/g-TOC, which has just entered the beginning of gas window. The  $\delta^{13}C_1$  value of the generated natural gas is between -36‰—-35‰, which obviously makes little contribution to the Yinan-2 gas pool. The Jurassic mudstone from Well Yinan-2 began to produce gas at 5 Ma and its present methane conversion rate reaches 0.32. Its  $\delta^{13}C_1$  value of the generated natural gas is between -37‰—-35‰. Obviously, it cannot be the main gas source rock. However, the Middle-Lower Jurassic coal measures are adjacent to the reservoirs, and have produced 54.4 mL/g-TOC, thus they have made some contribution to the Yinan-2 gas pool. The methane conversion rate of the Triassic mudstone from Well Yinan-2 is 0.2 and the yield of methane is 29 mL/g-TOC. Although the Triassic mudstone has entered the gas-generating stage, its  $\delta^{13}C_1$  value of the generated cumulative gas is between -43‰—-40‰, which is much lighter, and obviously different from the  $\delta^{13}C_1$  value of natural gas from the Yinan-2 gas pool.

In the center of Yangxia Sag, the yield of methane generated from the Middle-Lower Jurassic coal is 81 mL/

g-TOC and that of the Middle-Lower Jurassic mudstone is 130 mL/g-TOC. The  $\delta^{13}C_1$  value of natural gas generated from the Middle-Lower Jurassic coal is -33.5‰—-28.5‰ while that of the Middle-Lower Jurassic mudstone is -32‰—-17‰. Both of them are in the same range as the  $\delta^{13}C_1$  value of natural gas from the Yinan-2 gas pool. The time of gas generation from Triassic mudstone is earlier than that of the Middle-Lower Jurassic coal and mudstone. The present methane conversion rate of Triassic mudstone is up to 0.87. It has entered the main stage of gas generation. Geologically, trap formed at the Kangcun Formation ( $N_{1-2k}$ ) of Miocene-Pliocene (Zhao and Dai, 2002). Faults for gas migration formed between the Kuqa Formation ( $N_{2k}$ ) of Pliocene and the Xiyu Formation ( $Q_{1x}$ ) of Quaternary (5.3–0 Ma, Gao et al., 2002). However, the primary stage of gas generation from Triassic mudstone of Yangxia Sag occurred at 11–3Ma (Li, 2004). Obviously, most of the methane generated from Triassic mudstone lost. The  $\delta^{13}C_1$  value of natural gas generated at 5–0 Ma is between -36‰—-34‰, which is slightly lighter than the present  $\delta^{13}C_1$  value (-32.2‰) of natural gas from the Yinan-2 gas pool.

Therefore, the Middle-Lower Jurassic coal-bearing source rocks from the Yangxia Sag are the main gas sources of the Yinan-2 gas pool, which is consistent with the previous results (Li et al., 2001; Zhao et al., 2002).

According to the  $\delta^{13}C_1$  value of the Yinan-2 gas (-32.2‰), the Middle-Lower Jurassic source rock is regarded as the gas source rock of the Yinan-2 gas pool. Based on the theory of methane carbon isotope fractionation (Tang et al., 2000; Rooney et al., 1995), combined with the results of burial evolutionary history, thermal history and trap formation history (Zhao and Dai, 2002; Liang et al., 2002), the accumulating time and efficiency of natural gas in the center of Yangxia Sag are deduced as follows.

In the Yangxia Sag, natural gas from the Middle-Lower Jurassic coal accumulated at 5–0 Ma and its  $R_o$  values are 1.25%–1.95%. About 75% methane generated from Jurassic coal accumulates. Its loss rate of natural gas is about 25%. Natural gas from the Middle-Lower Jurassic mudstone accumulated during 5–0 Ma and its  $R_o$  values are 1.25%–1.90%. About 70%–75% methane generated from Jurassic mudstone accumulates. Its loss rate of natural gas is 25%–30%. Natural gas lost is the early generated low mature wet gas when the conversion rate of methane is 0.1–0.25. Thus, the Yinan-2 gas generally belongs to the cumulative gas since 5 Ma. This conclusion is consistent with the geological background.

On the basis of the above research, taking the Middle-Lower Jurassic coal-bearing source rocks for instance, a formation model of natural gas from the Yinan 2 gas pool is established (Fig. 6). Main characteristics are summed up as follows.

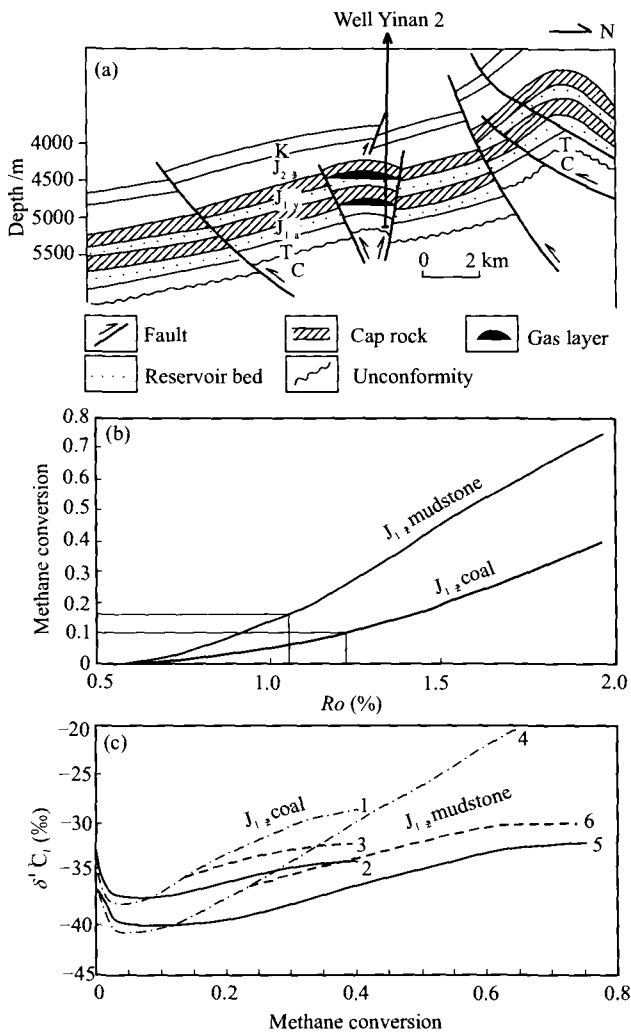


Fig.6. the formation model of natural gas in the Yinan 2 gas pool. Middle-Lower Jurassic coal: 1 - Instantaneous  $\delta^{13}C_1$ ; 2 - Cumulative  $\delta^{13}C_1$ ; 3 -  $\delta^{13}C_1$  of gas pool. Middle-Lower Jurassic mudstone: 4 - Instantaneous  $\delta^{13}C_1$ ; 5 - Cumulative  $\delta^{13}C_1$ ; 6 -  $\delta^{13}C_1$  of gas pool.

(1) The Yinan 2 gas pool primarily gathers natural gas, which is generated from the Middle-Lower Jurassic coal-bearing source rocks from the Yangxia Sag. Its main gas accumulation time is 5–0 Ma and the corresponding Ro value of gas source rock is 1.25%–1.95%.

(2) The loss rate of natural gas is 25%–30%. Natural gas lost is the early generated gas when the conversion rate of methane is less than 0.1–0.25.

(3) A small amount of wet gas generated from the Middle-Lower Jurassic coal measures source rocks of Well Yinan 2 might enter Yinan 2 gas pool, and thus they are the minor gas source.

(4) The pool-forming mode of natural gas generally belongs to the cumulative gas.

The formation model of natural gas from this gas pool not only complements and reduces the deficiencies of pool-forming model of natural gas, which traditionally depends

on the matching relationships of source rock, reservoir, cap rock and trap, but also is a useful reference in the study of other gas pools.

### 5 Conclusions

(1) The yield characteristics of gas generated from Jurassic and Triassic source rocks in the Kuqa Depression of Tarim Basin are studied through the thermal simulation experiments of gold tubes of closed-system. It is shown that gas yield is closely related to the pyrolysis temperature and the heating rate. It has proved that Jurassic coal-bearing source rocks have higher gas yields than Triassic source rocks.

(2) The kinetic parameters of gas generation and methane carbon isotopic fractionation from Triassic-Jurassic source rocks in the Kuqa Depression of Tarim Basin are obtained by using the KINETICS and GOR-ISOTOPE KINETICS software. These parameters are not only necessary for performing quantitative modeling of kinetic calculation, but also are important parameters for basin modeling, source rock assessment, hydrocarbon generation amounts calculation and resource prediction.

(3) It is demonstrated that there are differences in the kinetics parameters and the behaviours of gas generation, in the light of the kinetic calculation results of methane yields and carbon isotopic fractionation from Triassic-Jurassic source rocks in the Kuqa Depression, even for the same type III organic matter. So, different kinetic parameters of gas generation and methane carbon isotopic fractionation in different kinds of source rocks should be obtained.

(4) By using the Middle-Lower Jurassic coal-bearing source rocks as a representation, a formation model of natural gas from the Yinan-2 gas pool has been established, and also is a useful reference in the study of other gas pools. The source of natural gas of Yinan-2 gas pool is mainly from the Middle-Lower Jurassic coal-bearing source rocks, and generally belongs to the cumulative gas. Main gas accumulation time is 5–0 Ma and the corresponding Ro is in the range of 1.25%–1.95%. The loss rate of natural gas is 25%–30%.

### Acknowledgements

The authors are extremely grateful to Prof. Peng Ping'an, Prof. Liang Digang and Prof. Wang Zhaoming for their strong support. We thank Prof. Zhang Qimin, Prof. Liu Jinzhong, Prof. Bao Jianping, Prof. Wang Feiyu, Dr. Xiong Yongqiang, Dr. Hu Guoyi, Dr. Lu Hong, Dr. Liu Dayong, and Dr. Shui Yanhua for giving much help in sample preparation, experimental analysis and data processing. We also extend our thanks to those anonymous reviewers. The



manuscript is benefited greatly from their comments and suggestions. This research is financially supported by the National Natural Science Foundation of China (No. 40572085), Open Fund of State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences (No. OGL-200403), State Key Technologies R & D Program during the 10th Five-Year Plan Period (No. 2001BA605A02-03-01 and 2004BA616A02-01-01), New-century Excellent Talent Program of Ministry of Education (No. NCET-06-0204) and China Postdoctoral Science Foundation (No. 2002031282).

Manuscript received Jan. 23, 2007

accepted June 25, 2007

edited by Zhao Jie and Jiang Shaoqing

## References

- Behar, F., Vandenbroucke, M., Tang, Y., Marquis, F., and Espitalie, J., 1997. Thermal cracking of kerogen in open and closed systems: determination of kinetic parameters and stoichiometric coefficients for oil and gas generation. *Organic Geochemistry*, 26 (5 - 6): 321 - 339.
- Boreham, C. J., Horsfield, B., and Schenk, H. J., 1999. Predicting the quantities of oil and gas generated from Australian Permian coals, Bowen basin using pyrolytic methods. *Marine and Petroleum Geology*, 16: 165-188.
- Cramer, B., Faber, E., Gerling, P., and Krooss, B. M., 2001. Reaction kinetics of stable carbon isotopes in natural gas—insights from dry, open system pyrolysis experiments. *Energy & Fuels*, 15: 517-532.
- Cramer, B., Krooss, B. M., and Littke, R., 1998. Modeling isotope fractionation during primary cracking of natural gas: a reaction kinetic approach. *Chemical Geology*, 149: 235-250.
- Dai Jinxing, 1992. Identification of alkane gases. *Science in China (Series B)*, 34(2): 185-193.
- Dai Jinxing and Qi Houfa, 1989. The  $\delta^{13}\text{C}$ -Ro relationship of coal-derived hydrocarbon gases in China. *Chinese Science Bulletin*, 34(9): 690-692.
- Gao Gang, Huang Zhilong and Gang Wenzhe, 2002. The formation time of Yinan 2 gas pool in Kuqa Depression, the Tarim Basin. *Acta Paleogeography Sinica*, 4(2): 98-104 (in Chinese with English abstract).
- Gao Xilong, Xiao Xianming, Liu Zhongyun, Wang Jianbao, Gu Rutai, Lu Hongyou and Tang Yongchun, 2003. Hydrocarbon generation kinetics of source rocks in open system based on pyrolysis simulation experiment: a case study of the Dongying Depression. *Geochimica*, 32(5): 485-490 (in Chinese with English abstract).
- Jia Chengzao, 1997. *The Structure features and Hydrocarbon in the Tarim Basin*. Beijing: Petroleum Industry Press. 1-5 (in Chinese).
- Jia Chengzao, Qin Shengfei and Li Qiming, 2000. *Formation and distribution of coal-formed petroleum in the Kuqa foreland depression of Tarim Basin*. In: Dai Jinxing, Fu Chengde, Xia Xinyu (eds.), International Symposium on Hydrocarbon From Coal. Beijing: Petroleum Industry Press, 176-190 (in Chinese).
- Jia Chengzao, Hu Yunyang, Tian Zuojie and Li Qiming, 2001. *Exploration of large-sized gas fields in the Kuqa Depression of Tarim Basin*. In: Gao Ruiqi, Zhao Zhenzhang (eds.), *The Exploration on New Areas of Chinese Oil and Gas (Vol. 1)*. Beijing: Petroleum Industry Press. 1-54 (in Chinese).
- Li Jian, Xie Zengye, Li Zhisheng, Luo Xia, Hu Guoyi and Gong Se, 2001. The source correlation of natural gas in Kuqa Depression of the Tarim Basin. *Petroleum Exploration and Development*, 28(5): 29-32 (in Chinese with English abstract).
- Li Xianqing, Xiao Xianming, Tang Yongchun, Mi Jingkui, Xiong Bo and Bao Jianping, 2003a. The origin evaluation of natural gas with the modeling of carbon isotope kinetics. *Chinese Petroleum Exploration*, 8(4): 50-55 (in Chinese with English abstract).
- Li Xianqing, Xiao Xianming, Mi Jingkui and Wang Feiyu, 2003b. New advance in kinetic model of stable carbon isotope ratio in natural gas. *Fault-Block Oil and Gas Field*, 10(3): 1-4 (in Chinese with English abstract).
- Li Xianqing, 2004. Research and application of hydrocarbon generation kinetics of natural gas. Research report of postdoctoral work. Guangzhou: Guangzhou Institute of Geochemistry, Chinese Academy of Sciences. 16-98 (in Chinese).
- Li Xianqing, Xiao Xianming, Tian Hui, Tang Yongchun, Fang Jiahu and Zhou Qiang, 2005. The modeling of carbon isotope kinetics and its application to the evaluation of natural gas. *Earth Science Frontiers*, 12(4): 543-550 (in Chinese with English abstract).
- Li Xianqing, Xiao Xianming, Tang Y., Xiao Zhongyao, Mi Jingkui, Liu Dehan, Shen Jiagui and Liu Jinzhong, 2006. *The generation and accumulation of Natural gas from Kela-2 Gas Field in Tarim Basin, NW China*. In: Chou Chenlin, Dai Shifeng, and Jin Kuili (eds.), *Abstract of the 23rd Annual Meeting of the Society for Organic Petrology*. Beijing: China University of Mining and Technology, 23: 129-130.
- Liang Digang, Zhang Shuichang, Jin Zhijun, Zhang Baomin, Zhao Mengjun, Wang Feiyu and Sun Yongge, 2000. *Sources and formations of oil & gas in the Tarim Basin*. A research report of the "9th Five-Year Plan Period" State Key Scientific Project (99-111-01-03). Beijing: Research Institute of Petroleum Exploration and development, Petrol-China. 132-166 (in Chinese).
- Liang Digang, Zhang Shuichang, Chen Jianping, Wang Peirong and Wang Feiyu, 2002. *Geochemistry of hydrocarbon in Kuqa depression, Tarim basin*. In: Liang Digang, Huang Difan, Ma Xinhua, Li Jingming (eds.), *New Advances on Organic Geochemistry: The 8th Chinese Academic Symposium of Organic Geochemistry*. Beijing: Petroleum Industry Press. 22-42 (in Chinese).
- Liang Digang, Zhang Shuichang, Chen Jianping, Wang Feiyu and Wang Peirong, 2003. Organic geochemistry of oil and gas in the Kuqa depression, Tarim Basin, NW China. *Organic Geochemistry*, 34: 873-888.
- Liu Jinzhong and Tang Yongchun, 1998. One example of predicting methane generation yield by hydrocarbon generating kinetics. *Chinese Science Bulletin*, 43(11): 1187-1191.
- Liu Jinzhong, 2002. *Hydrocarbon generation kinetics of kerogen and its geological application*. In: Liang Digang, Huang Difan, Ma Xinhua, Li Jingming (eds.), *New Advances on Organic Geochemistry: The 8th Chinese Academic Symposium of Organic Geochemistry*. Beijing: Petroleum Industry Press. 343-351 (in Chinese).

- Lorant, F., Prinzhofer, A., Behar, F., and Huc, A. Y., 1998. Carbon isotopic and molecular constraints on the formation and the expulsion of thermogenic hydrocarbon gases. *Chemical Geology*, 147: 249–264.
- Lu Shuangfang, 1996. *Hydrocarbon generation kinetics of organic matter and its application*. Beijing: Petroleum Industry Press. 15–54 (in Chinese).
- Lu Shuangfang, Fu Xiaotai, Li qiming, Liu Xiaoyan and Feng Yali, 2000. The renew and significane of original parameters of hydrocarbon generation kinetic model from matured organic matter in Tarim Basin. *Geological Review*, 46(5): 556–560 (in Chinese with English abstract).
- Mei Mingxiang, Yu Bingsong and Jin Weiguang, 2004. Sequence stratigraphy of the desert system: a case study of the Lower Cretaceous in the Kuqa Basin in Xinjiang, Northwestern China. *Acta Geologica Sinica* (English edition), 78(3): 744–755.
- Qin Shengfei, 1999. The origin of abnormal natural gas in the Kuqa Depression, Tarim Basin. *China Petroleum Exploration*, 4(3): 21–23 (in Chinese with English abstract).
- Rooney, M. A., Claypool, G. E., and Chung, H. M., 1995. Modeling thermogenic gas generation using carbon isotope ratios of natural gas hydrocarbons. *Chemical Geology*, 126: 219–232.
- Song Yan, Jia Chengzao, Zhao Mengjun and Tian Zuoji, 2002. Controlling factors for large gas field formation in thrust belt of Kuqa coal derived hydrocarbon foreland basin. *Chinese Science Bulletin* (supp.), 47: 64–69.
- Tang, Y., Perry, J. K., Jenden, P. D., and Schoell, M., 2000. Mathematical modeling of stable carbon isotope ratios in natural gases. *Geochimica et Cosmochimica Acta*, 64 (15): 2673–2687.
- Ungerer, P., amd Pelet, R., 1987. Extrapolation of the kinetics of oil and gas formation from laboratory experiments to sedimentary basins. *Nature*, 327: 52–54.
- Wang Feiyu, Zhang Shuichang, Zhang Baomin and Zhao Mengjun, 1999. Organic maturity of Mesozoic source rocks in Kuqa Depression, Tarim Basin. *Xinjiang Petroleum Geology*, 20 (3): 221–224 (in Chinese with English abstract).
- Wang Zhaoming, Wang Tingdong, Xiao Zhongyao, Xu Zhiming, Li Mai and Lin Feng, 2002. Migration and accumulation of natural gas in Kela-2 gas field. *Chinese Science Bulletin* (supp.), 47: 103–108.
- Wei Guoqi, Jia Chengzao, Shi Yangshen, Lu Huaifu and Wang Liangshu, 2000. The Structure features and Hydrocarbons in the Tarim Cenozoic rejuvenation foreland Basin. *Acta Geologica Sinica*, 74(2): 123–133 (in Chinese with English abstract).
- Xiong Yongqiang, Geng Ansong, Wang Yunpeng, Liu Dehan, Jia Rongfen, Shen Jiagui and Xiao Xianming, 2002. Kinetic simulating experiment on the secondary hydrocarbon generation of kerogen. *Science in China* (Series D), 45(1): 13–20.
- Xu Yongchang, Shen Ping, Liu Wenhui, Chen Jianfa and Tao Mingxing, 1994. *The genetic theory of natural gas and its application*. Beijing: Science Press, 45–81 (in Chinese).
- Zhao Jinzhou and Dai Jinxing, 2002. The time and history of natural gas formation in Kuqa Foreland Thrust Belt. *Acta Petrolei Sinica*, 23(2): 6–10 (in Chinese with English abstract).
- Zhao Mengjun, Lu Shuangfang and Li Jian, 2002. The geochemical features of natural gas in Kuqa depression and the discussion on the gas source. *Petroleum Exploration and Development*, 29 (6): 4–7 (in Chinese with English abstract).
- Zhou Xingxi, 2001. The reservoir-forming process and model in the Kuqa petroleum system. *Petroleum Exploration and Development*, 28(2): 8–10 (in Chinese with English abstract).