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Thermal cracking history by laboratory kinetic simulation of Paleozoic oil in eastern Tarim Basin, NW China, implications for the occurrence of residual oil reservoirs

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Abstract

The thermal stability of Paleozoic oil in eastern Tarim Basin, NW China was investigated through laboratory kinetic simulation experiments. Laboratory cracking of a selected marine oil sample from Ordovician strata in well LG-1 of Tarim Basin was performed by confined, dry pyrolysis system at $T = 300$–650 °C, $P = 50$ MPa. Results indicated the oil required higher temperature for cracking. At laboratory heating rates, oil cracking started at 390–400 °C and the laboratory cracking was completed at around 650 °C. At geological heating rates, the onset temperature is about 148–162 °C for cracking start and was completed at 245–276 °C. The oil-cracking history was recovered using the acquired kinetic parameters and the geothermal history of TD-2, and the threshold temperature for oil cracking under geological conditions was calculated. The oil cracking started at 165 °C ($R_o = 1.45\%$) and stopped in early Devonian (390 Ma), and the oil-cracking rates in the strata of $\in$-O_1 reached 60–70% at the end of Silurian. The calculated oil generation and oil cracking windows overlapped to some extent and were completed rapidly. The possible geological controls for the occurrence of residual oil reservoirs in Eastern Tarim basin have been discussed, including the high stability of the Paleozoic oil in Tarim Basin, the fast heating rate and longer duration time for oil cracking, the slight biodegradation in later uplift, the good preservation of the paleo-reservoirs and the moderate structural adjustment, which were critical for the exploration of residual oil and gases in this area.

1. Introduction

The Lower Paleozoic strata ($\in$-O_1) in eastern Tarim Basin, NW China contain eminent petroleum source rocks due to their good biogenetic origins (Type I/II kerogen), huge thickness (accumulative

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sedimentary thickness of ϵ-O_1 strata in Manjaer Depression reaches 8000 m, Zhang et al., 2004a) and high TOC concentration (2.84% average from Sun et al., 2003). The exploration of the Paleozoic strata is focusing on the cracking gases in this area because of the high maturity-levels (>2.0% R_o). Because the oil-bearing strata (ϵ-O_1) experienced very high temperature (>190–200 °C) during maturation, it is generally assumed that oil accumulations have been destroyed by thermal stress. Other possible destructive factors to old oil reservoirs include biodegradation and evaporative fractionation caused by the structural uplift in Hercynian and Indosinian orogenies. The discovery of residual oil in well TD-2 at the end of 2001, which was generated very early (>400 Ma) and experienced very high thermal alteration ($T > 200$ °C), arouses the exploration expectation of oil reservoirs in this area. However, the key to the occurrence of residual oil reservoir in this area is to study the oil thermal stability and the oil cracking history.

Laboratory pyrolysis methods have been widely used to study the thermal stability of oil, to compare compositional changes with increasing thermal stress, and to determine the process of oil to gas cracking kinetically in particular (Bjorøy et al., 1988; Ungerer et al., 1988; Behar et al., 1991, 1992; Horsfield et al., 1992; Kuo and Michael, 1994; Pepper and Dodd, 1995; Schenk et al., 1997; Tsuzuki et al., 1999; Hill et al., 2003). Previous studies show that oil cracking is a complicated, dynamic and progressive process involving many different simultaneous cracking reactions of the high molecular weight hydrocarbons and heteroelement (N, S, O) compounds to low molecular weight compounds (condensate and gas) and pyrobitumen (Hill et al., 2003). For oil thermal stability, early work suggested oil was only stable to 150 °C (McNab et al., 1952; Barker, 1990; Hayes, 1991). However, fieldwork (Price et al., 1979, 1981; Price, 1981; Mango, 1990; Horsfield et al., 1992; Schenk et al., 1997), laboratory work (Dominé, 1989, 1991; Dominé and Enguehard, 1992; Horsfield et al., 1992; Price, 1995; Schenk et al., 1997) and theoretical calculations (Dominé et al., 1990, 1998) suggest that oil is stable to 200 °C. In order to study the thermal stability of Paleozoic oil, laboratory pyrolysis experiments were performed and the kinetic parameters of the cracking of gaseous hydrocarbon (C_{1-5}) from a selected marine oil sample were derived by using a confined system. The threshold temperature for oil cracking and cracking-R_o (%) pattern under geological conditions were calculated. After recovering the oil-cracking history using the geothermal history in the site of Well TD-2, the possible geological controls for the occurrence of residual oil reservoirs in this area were discussed.

2. Study area and geological setting

The wells TD-1 and TD-2 are situated in TD lower-bulge, eastern section of Central Uplift (TZ Uplift) of the southern edge of Manjaer Depression, Tarim Basin (Fig. 1). TD-2 structure began to uplift in the Devonian–Triassic Period, so Devonian–Triassic strata were not deposited. The deposited Upper Ordovician and Silurian strata (O_{2+3}–S) were eroded completely, and the Lower Ordovician stratum (O_1) also underwent severe erosion. With a thickness of 56 m, the Lower Ordovician stratum (Hetuwa Formation, O_{1h}) is a series of black mudstone and argillite deposited in a deep starved basin. The average TOC of O_{1h} is 3.07% and the maximum TOC reaches 7.2% (23 samples). The upper part of the Cambrian strata is composed of argillaceous-limestone deposited in the slope area of the platform edge and their thickness reaches 272 m. The lower part of the Cambrian strata is composed of dark mudstone and shale deposited in a deep starved basin. The average TOC of the Cambrian rocks is 1.45% and the maximum TOC reaches 4.88% (55 samples). The maturity level of the Lower Paleozoic rocks is very high, ranging from 2.05% to 2.12% (equivalent R_o%) for Upper Ordovician rocks, 2.44–2.65% for Lower Ordovician rocks and 2.67–2.75% for Cambrian rocks (Sun et al., 2003; Zhang et al., 2004a). The present hydrocarbon potentials of these rocks are very low and the Rock-Eval index of $S_1 + S_2$ is less than 0.1 mg/g due to their very high maturities (Zhang et al., 2004a).

TD-2 experienced very fast burial and uplift. Fig. 2 shows the burial history of TD-2. It may be observed that fast burial took place from the Ordovician to the Silurian period and that the deepest burial was attained in the Silurian (>6000 m). From the Devonian to the Triassic periods, the strata were uplifted continuously which made the O_{2+3}–S strata experience severe erosion. The residual thickness of the O_{2+3} is 1678 m in TD-2. It was reported that the average sedimentary O_{2+3} thickness was 6000–8000 m in this area (Zhang et al., 2000a). After correlating with other wells, it was estimated that the eroded thickness of O_{2+3} strata was about 3800 m (Zhang et al., 2000b; Zhang et al., 2004a).

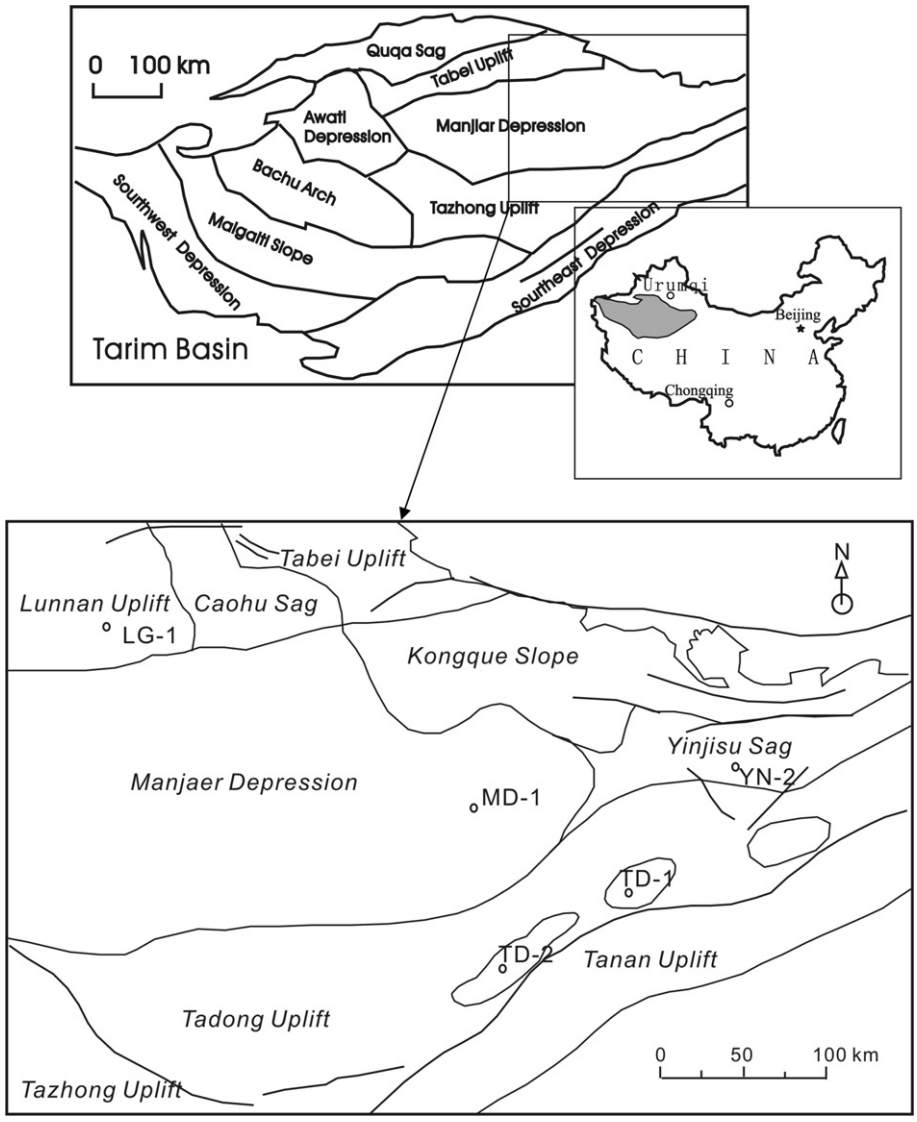

Fig. 1. Map of Tarim Basin showing the tectonic units of the study area including Tadong Uplift, Manjaer Depression and Yinjisu Sag, distribution of TD structure and well TD-1, TD-2, MD-1, LG-1 and YN-2 (minor modification from Zhang et al. (2004a)).

The present exploration has not found any commercial gas production in well TD-2 while a small quantity of oil has been discovered. The oil of the TD-2 is produced from fractured limestone over the depth range of 4630–4670 m, the top of the Cambrian. The crude oil of TD-2 is typical viscous oil, with a density of the drill stem test oil of 1.0217 g/cm^3 (API = 7°) and the viscosity is 2698 MPa s. The bulk geochemical characteristics of the oil are as follows: wax content is 10.64%, resins + asphaltenes is 45.91% and saturates is 24%. TD-2 oil has a full *n*-alkane distribution and the peak carbon is C_{13} (Fig. 3). The calculated C_{21-}/C_{21+} value is 5.17, OEP is 1.08, Pr/Ph is 1.24, Pr/*n*-C_{17} is 0.67 and Ph/*n*-C_{18} is 0.59. The bulk carbon isotope ($\delta^{13}C_{oil}$) is about −28.2‰ which is about 4‰ heavier than that of normal marine oil in Tarim Basin (Sun et al., 2003; Zhang et al., 2004a). These properties demonstrate a typical residual oil after high thermal alteration, which can be supported by the presence of abundant high-maturity ($BR_o\% = 2.7$–5.0%) pyrobitumen in Cambrian strata of TD-2, the high homogenization temperature of coeval aqueous brine inclusions with gaseous inclusions reaching 160–220 °C (Sun, 2003, private communication; Zhang et al., 2004a). And

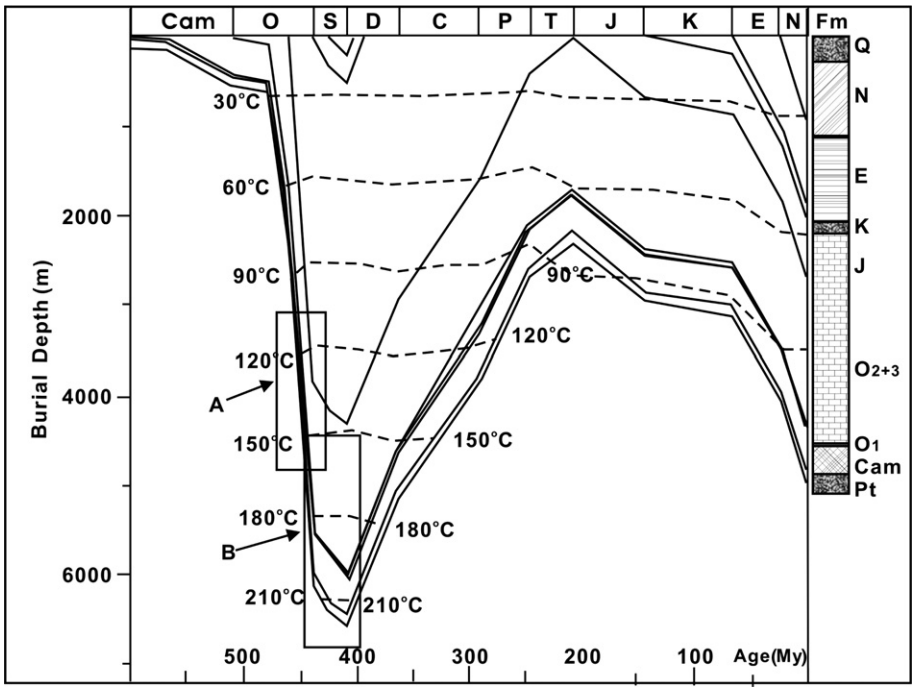

Fig. 2. The burial history, paleo-temperature and maturity history of Well TD-2, Tarim Basin labeled W the oil generation (A) and oil cracking (B) windows.

the identification of high weight polycyclic aromatic hydrocarbons in TD-2 oil indicates that TD-2 oil has experienced severe thermal alteration (Simoneit and Fetzer, 1996; Sun, 2003, private communication).

3. Sample and methods

3.1. Sample

The oil sample selected for the experiment was drill stem test oil from the Ordovician reservoir at the depth of 4010 m of well LG-1 in Lunan Uplift, north of Manjar Depression, Tarim Basin (Fig. 1), which is a typical representative for normal Paleozoic marine-sourced oil in the Tarim Basin. Just like the oil in TD-2, this oil sample originated from the Cambrian source rock in Manjaer Depression (Zhao et al., 2001). Although, the location of this oil sample is 300 km away from the TD-2, it has been reported that this oil can be correlated to the oils from TD area (Ma et al., 2005). The basic geochemical data of the oil sample are listed in Table 1.

The pyrolysis device used is a closed, temperature programmed, gold-tube system similar to those described by Burnham et al. (1987, 1988), Behar et al. (1992, 1995, 1997, 1999), Tang et al. (1991), Tang and Stauffe (1994, 1995), Liu and Tang (1998) and Lorant and Behar (2002). The reason for not using an open system is that the pyrolysis of oil is very difficult in open system, especially in high temperature ranges. In contrast to MSSV, the gold-tube system can be conducted under near-natural pressure.

Kinetic pyrolysis experiments were carried out in gold tubes (50 mm length, 5 mm internal diameter and 0.5 mm thick), sealed by welding under an argon atmosphere containing between 30 and 60 mg of oil sample. The gold tubes were placed in pressurized autoclaves and kept at a pressure of 50 MPa during the experiment. The temperature was measured with an accuracy estimated to be ±1 °C, by a thermocouple placed in an empty cell inside the autoclave (Liu and Tang, 1998). About 12–16 temperature points were set from 300 to 650 °C with three constant heating rates (2 °C/h, 6.3 °C/h and 20 °C/h). Tubes containing oil were placed into different cells. The cell was taken out quickly and cooled after a designed temperature point had been reached. Each tube, after cleaning, was weighed in order to detect any mass loss due to the possible leakage during the experiment. The

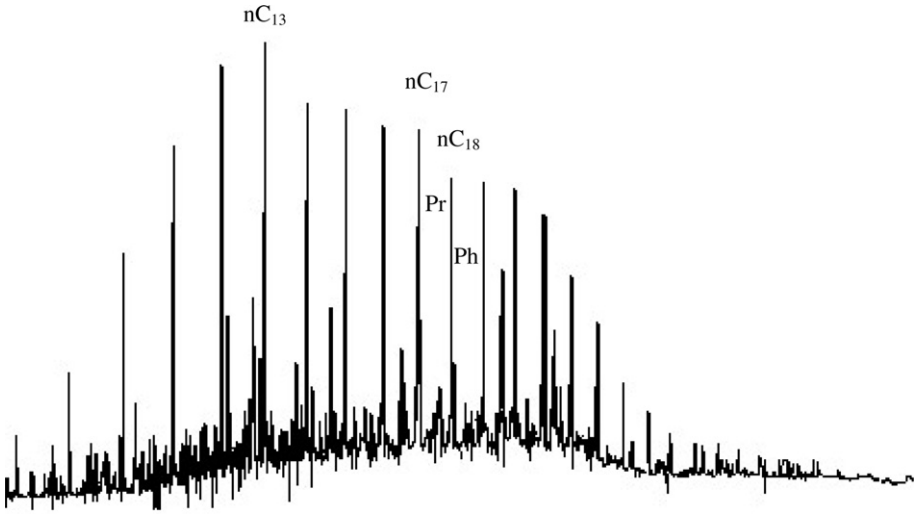

Fig. 3. Gas-chromatogram of whole oil in well TD-2, Tarim Basin.

cooled gold tube was placed in a vacuum glass piercer, which was connected to a Toepler pump and a volume-calibrated glass pipe through vacuum line (see Behar et al. (1992) for detailed description of the Toepler pump). The gold tube was pierced by steel needle in vacuum (with the pressure of $<10^{-5}$ MPa), and all of the gaseous hydrocarbons were concentrated by the Toepler pump into the volume-calibrated pipe for volume quantification. The pipe was connected to an HP 6890 gas chromatograph (GC) through a valve for the on-line gaseous hydrocarbon analysis. The hydrocarbons were quantified using an external standard. The detailed analysis procedure has been reported by Liu and Tang (1998) and Xiong et al. (2001).

3.2. Modeling of kinetic parameters

The cumulative kinetic parameters were determined and computed using commercial software KINETICS2000™ developed by Lawrence Livermore National Laboratory (LLNL) and Humble Instruments & Services, Inc. The processing options within the KINETICS 2000™ include the models of Approximate, Friedman, Discrete, Gaussian, 1st or Nth order, Weibull, Nucleation (3 Parameters) and Alternate Pathway (detailed description could be found on http://www.humble-inc.com/k2000.htm). The discrete model was adopted in this study due to its good fit with the closed system experimental data (e.g., Burnham and Happe, 1984; Burnham et al., 1987, 1988, 1996; Behar et al., 1992, 1995, 1997; Tang et al., 1991; Tang and Stauffe, 1994, 1995; Liu and Tang, 1998; Lorant and Behar, 2002).

4. Results

4.1. Laboratory pyrolysis

Laboratory closed-system pyrolysis could potentially provide useful information about the gaseous hydrocarbon generation of oil cracking. For studying the oil stability, we analyzed the gaseous hydrocarbons which were cracked from the oil. The yields of hydrocarbon gases (C_{1-5}), obtained from cracking of the Paleozoic oil from the Tarim Basin at different heating rates are summarized in Table 2 and Fig. 4. From Fig. 4, it appears that the maximum cumulative yields of gases (C_{1-5}) are roughly com-

Table 1
Sample of simulation experiment and its geochemical data

Areas	Depth (m)	Type	Age	API (°)	CPI	SAT (%)	ARO (%)	ASPH (%)	RESIN (%)
Well LG-1, Tarim Basin	4010	Normal marine oil	Є-O	36.5	1.09	61.2	22.8	10.8	5.2
				Pr/Ph	Pr/n-C_{17}	Ph/n-C_{18}	OEP	S (%)	$\delta^{13}C_{oil}$ (‰)
				1.07	0.33	0.37	0.98	0.17	−33.2

Table 2
Cumulative yields (ml/g sample) of cracking gaseous hydrocarbon (C_1–C_5) from Paleozoic oil of Tarim Basin at heating rates of 20 °C/h, 6.3 °C/h and 2 °C/h

Heating rate					
20 °C/h		6.3 °C/h		2 °C/h	
Temperature (°C)	C_1–C_5 (ml/g)	Temperature (°C)	C_1–C_5 (ml/g)	Temperature (°C)	C_1–C_5 (ml/g)
406.1	3.35	406.2	28.603	406.3	53.857
429.9	27.529	430.2	93.434	430.4	159.340
455.4	106.357	455.2	205.630	455.0	304.904
476.7	242.867	477.7	322.245	455.0	295.607
503.4	359.086	477.7	321.876	479.6	401.624
527.6	430.362	503.5	412.282	504.7	465.478
527.6	433.123	530.2	488.758	504.7	458.000
550.9	491.481	558.0	531.710	535.0	547.154
550.9	488.928	558.0	532.005	565.0	541.940
575.1	543.462	599.9	570.977	600.6	554.659
599.1	569.517	599.9	571.298	600.6	558.338
625.0	603.613	622.5	584.738	620.0	515.864

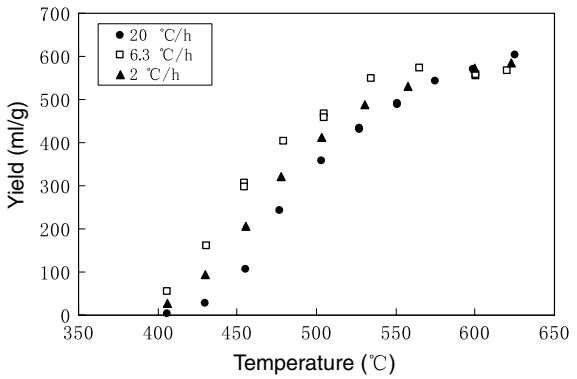

Fig. 4. Cumulative yields (ml/g sample) of cracking gaseous hydrocarbon (C_1–C_5) from Paleozoic oil in Tarim Basin versus pyrolysis temperature (°C) at heating rates of 20 °C/h, 6.3 °C/h and 2 °C/h.

parable among the different heating rates. The plateau in the cumulative yields marks the end of hydrocarbon generation (Schenk and Horsfield, 1993; Dieckmann et al., 1998, 2000), and the gaseous hydrocarbon generation from the oil is clearly determined by the maximum yields at different heating rates. For the Paleozoic oil from Tarim Basin used in this study, the C_{1-5} potential reaches 604 ml/g, which represents the amount of gases formed from the complete oil cracking in the laboratory. The laboratory pyrolysis results indicated that the oil required high temperature for its cracking. For example, oil began to crack at 390–400 °C at laboratory heating rates (2–20 °C/h), the oil-cracking rate reached 75% at 550 °C, and the laboratory temperature was about 650 °C when complete cracking was achieved.

4.2. Kinetic parameters

Bulk kinetic parameters of gaseous hydrocarbons (C_{1-5}) obtained from this experiment are different from those obtained in an open system. However, they appear effective in evaluating the gas generation from oil cracking (Burnham et al., 1987, 1988; Ungerer, 1990; Behar et al., 1997; Boreham et al., 1999; Dieckmann et al., 1998, 2000). We used the KINETICS™ package to derive kinetic parameters including activation energy distributions and frequency factor for the C_{1-5} from the oil sample under investigation. The gas yields were normalized before the kinetic calculation. The best-fit between the experimental and calculated data and the results of the discrete activation energy distributions (E_a) and frequency factors (A) of C_{1-5} from the studied marine oil sample are shown in Fig. 5. Clearly, the kinetic parameters of oil cracking exhibited a relatively high activation energy (E_a) (Fig. 5), which ranged from 58 to 76 kcal/mol (with $A = 4.5 \times 10^{14}\ s^{-1}$). From the E_a distribution, it was found that there were two types of gas precursors. Type 1 has lower E_a, which is less than 64 kcal/mol and accounts for 64.12% of the total cracking potential, and type 2 has higher E_a, which is larger than 67 kcal/mol and accounts for 35.89% of the total cracking potential (Fig. 5).

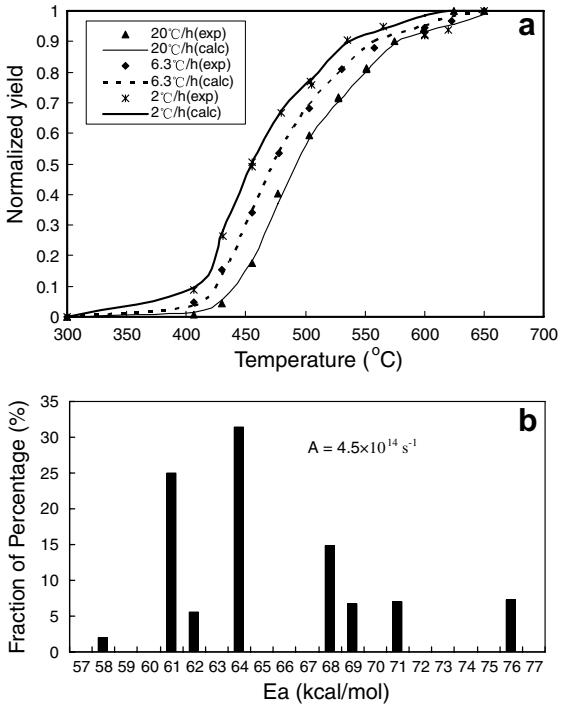

Fig. 5. Experimental and calculated gaseous hydrocarbon (C_1–C_5) yields (normalized) at heating rates of 20 °C/h, 6.3 °C/h and 2 °C/h (a) and discrete activation energy distribution and frequency factor (b) of Paleozoic oil sample from Tarim Basin. (exp: experimental, calc: calculated).

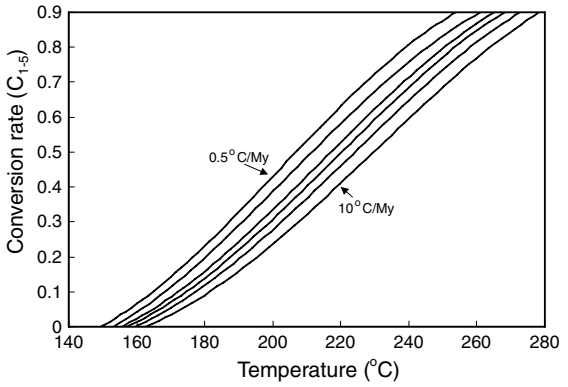

Fig. 6. The conversion rate of cracked gas from Paleozoic oil in Tarim Basin at geological temperature and geological heating rates (lines from left to right corresponding to 0.5, 1, 2, 3, 5, 10 °C/Ma).

5. Discussion

5.1. Thermal stability of Paleozoic oil in Tarim Basin

The laboratory pyrolysis results have shown the required temperatures for cracking of Paleozoic oil, Tarim Basin (Fig. 5). For studying the thermal stability of Tarim Basin Paleozoic oil under geological conditions, a series of heating rates including 0.5, 1, 2, 3, 5 and 10 °C/Ma were used to derive the extrapolations for the required geological temperature of oil cracking. The conversion rate of cracked gas from oil under geological temperatures and geological heating rates are shown in Fig. 6. It is clear that the threshold temperature for cracking is about 148–162 °C and the temperature for complete cracking is about 245–276 °C under geological conditions (Fig. 6). These results demonstrated a relatively high stability of the Early Paleozoic oil in Tarim Basin. It is also clear that the faster the geological heating rates are, the higher the required geological temperatures are for oil cracking. We will discuss the relationships between the geological heating rates and the required geological temperatures for oil cracking in following sections by combining the results at constant geological heating rates with the results from real geothermal history from Well TD-2.

5.2. Oil thermal cracking history in TD-2

According to Sun et al. (2003) and Zhang et al. (2004), the burial history of ϵ-O_1 source rocks (Fig. 2) is characterized by two features. The first one was fast burial during Ordovician to Silurian with the maximum burial depth of 6000 m in the Silurian (Fig. 2), and the second one was the continuous uplift from the early Devonian to the Triassic with the deduced erosion thickness of 4300 m for O_3–S strata. The present residual thickness of O_{2-3} is 1678 m in TD-2; however, the present thickness of the corresponding strata in the east of Manjar Depression is about 6000–8000 m (Zhang et al., 2000b; Sun et al., 2003). Therefore, it was estimated that the deposited thickness of O_{2-3} was more than 5000 m in TD-2, which made the strata of ϵ-O_1 quickly buried to depths of more than 6000 m, the temperature increased from 30 to 210 °C and the R_o% increased from 0.5% to 2.6–3.0% (Fig. 7). Here, the maturities of the rocks were calculated using the equivalent Easy R_o% (Sweeney and Burnham, 1990) and calibrated by the measured maturities. The thermal history at the TD-2 site was determined by combining the burial history and maturation history restrained by real maturity measurements (Fig. 7). It could be found that the maturation of the ϵ-O_1 source rocks was finished at the

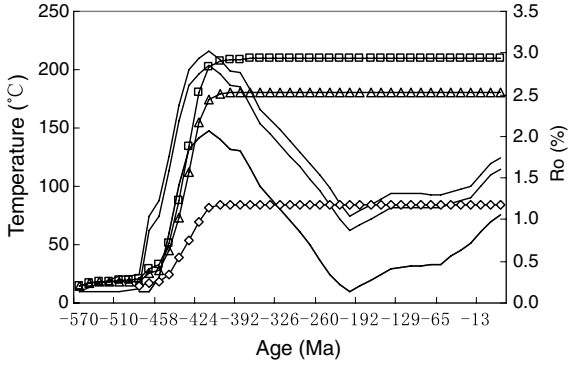

Fig. 7. The thermal and maturation history of Well TD-2, Tarim Basin (Line: temperature; Line with symbols: R_o (%); The simulation layers include the bottom and the top of Cambrian and Ordovician strata).

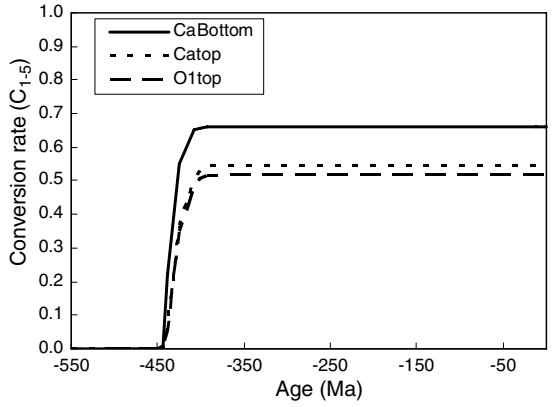

Fig. 8. Conversion rate of cracking gas from oil of TD-2 under geological history (Ca: Cambrian strata; O_1: lower Ordovician; O_{23} middle–upper Ordovician).

end of the Silurian. The fast maturation of the source rocks was accompanied by oil generation and cracking. The main oil generation time was calculated in later Ordovician (440–450 Ma) by 1-D basin model (Fig. 7) and it was calibrated by the homogenization temperature of coeval aqueous brine inclusions with oil inclusions (Sun et al., 2003; Zhang et al., 2004a). The unique characteristics of the earlier Paleozoic deposition in eastern Tarim Basin made the hydrocarbon generation very early (440–450 Ma) and very fast (10 Ma duration). The filled solid bitumen in earlier Caledonian structural fractures of reservoir rocks suggested that the TD-2 was a very old oil reservoir formed in later Ordovician (Sun et al., 2003; Zhang et al., 2004a,b). An old oil reservoir with more than 400 Ma preservation provides us a very good case for studying destruction and preservation of oil. Here, we took the yields of cracking gaseous hydrocarbons (C_1-C_5) as an indicator of the cracking degree of the oil. The cracking rate of oil in TD-2 site was calculated using the acquired kinetic parameters and the thermal history of ϵ-O_1 strata in Fig. 6. The conversion rate of cracking gas from oil of TD-2 in geological history is shown in Fig. 7. The oil-cracking rate in the strata of ϵ-O_1 reached 60–70% at the end of the Silurian (Fig. 8). The oil cracking stopped as the strata uplifted in the early Devonian (390 Ma).

For studying the precise cracking history of the oil in TD-2, the relations between oil-cracking rate and maturity and the threshold temperature for the oil cracking in TD-2 were also computed (Fig. 9a and b). The oil cracking started at a temperature of 165 °C ($R_o = 1.45\%$) at the TD-2 site. Obviously, the cracking temperature is quite high, which reflects the fast heating rate and high oil stability in this site.

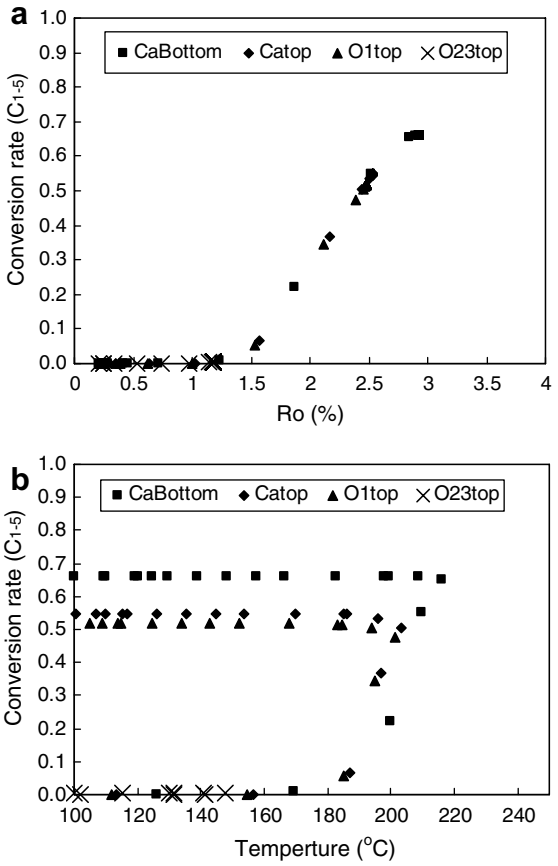

Fig. 9. Relations between oil-cracking rate and maturity (a, EasyR_o%) and the threshold temperature (b) for the oil cracking in TD-2.

For showing the relationships between oil generation and oil cracking during burial, we calculated the oil generation window by using the optimized kinetic parameters proposed by Pepper and Corvi (1995) for marine clastic deposition with moderate sulfur content, which were quite similar to the depositional environment of $\in$-O_1 strata in TD-2, including mean activation energy ($E_{mean} = 215.2$ kJ mol^{-1}, $\sigma = 8.3$ kJ mol^{-1}) with the frequency factor ($A = 8.14 \times 10^{13}$ s^{-1}). Here a fractional real heating rate of the fast burial stage in TD-2 was calculated to be about 3.56 °C/Ma, which was used for further calculations. The kinetic parameters derived in this study were used for calculating the cracking window of TD-2 by using the heating rate of 3.56 °C/Ma. Following Pepper and Corvi (1995), the oil window was determined between the generation rates from 0.1 to 0.9, and the oil-cracking window was determined between the oil-cracking rates from 0.1 to 0.9. The calculated oil generation window was from 108 to 177 °C and the oil-cracking window was from 165 to 258 °C for the heating rate of 3.56 °C /Ma in TD-2. These results were also labeled in the burial history profile (Fig. 2), which clearly indicated that the oil generation and oil cracking windows overlapped to some extent and were completed in a very short time. The calculated results show that the oil-cracking windows for the bottom of Cambrian strata ($\in$) began at 443 Ma and ended at 401 Ma, and the oil-cracking windows for the top of lower Ordovician strata (O_1) began at 438 Ma and ended at 391 Ma (Figs. 2 and 9). Compared with the duration of the oil generation window (10 Ma, from 450 Ma to 440 Ma), the duration of the oil-cracking window was relatively long, 42–47 Ma.

5.3. Implications for the occurrence of residual oil reservoirs

The above laboratory-based simulation results in TD-2 can provide some information and implications for the occurrence of residual oil reservoirs in eastern Tarim Basin.

Firstly, the Paleozoic oil in Tarim Basin has very high thermal stability. The required temperatures for oil cracking at both laboratory and geological heating rates are very high. The activation energies (E_a) of oil cracking are also relatively high. It is a key for the long-term preservation of the oils experiencing the high geological temperatures like TD-2.

It is well known from chemical kinetics that the heating rate is an import factor to control oil cracking. Faster heating rates require higher geological temperatures for oil cracking. The relationship between geological heating rates and cracking-window duration (Ma) for Paleozoic oil in eastern Tarim Basin was calculated from the laboratory results and plotted in Fig. 10. The arc line representing the duration time for complete cracking of the oil clearly demonstrates the evolution trend as the geological heating rates change. The average heating rate in the process of fast burial of TD-2 was calculated from the thermal history data (Fig. 7) that was about 3.56 °C/Ma (labelled in Fig. 10). It can be found that the duration time for the complete oil cracking in the heating rate of TD-2 site (3.56 °C/Ma) is about 66.9 Ma (horizontal line A in Fig. 10). However, the real duration time of the oil-cracking window for $\in$-O_1 strata in TD-2 is in the range of 32.3–36.6 Ma (horizontal lines B and C in Fig. 10). The duration time of oil-cracking window in TD-2 is not sufficient for the complete oil cracking. It is another reason that the oil in TD-2 can survive.

Biodegradation is another key control for the oil preservation. From Fig. 2, it can be found that there occurred a fast uplift from Devonian to Triassic, and the uplift height exceeded 4000 m. It has been reported that TD-2 oil has experienced biodegradation confirmed by the presence of 25-norhopanoids in the TD-2 oil (Sun et al., 2003; Zhang et al., 2004a). Obviously, the biodegradation is not as severe as in other lower Paleozoic reservoirs in

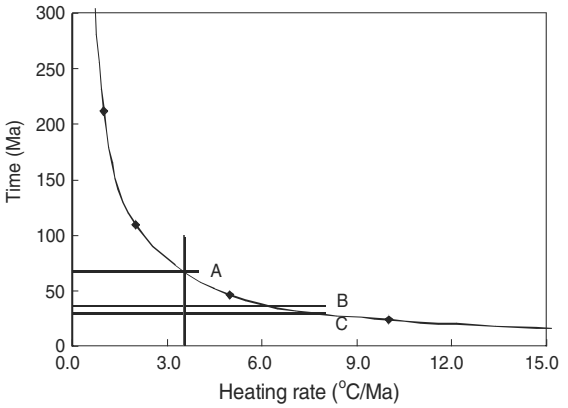

Fig. 10. Relationship between geological heating rates and cracking-window duration (Ma) of Paleozoic oil in Eastern Tarim Basin. (The arc line representing the duration time for complete cracking of the oil versus geological heating rates; A: duration time for the complete oil cracking at the heating rate of TD-2 site; B and C: the real duration time range of the oil-cracking window for $\in$-O_1 strata in TD-2 site.)

central Tarim Basin, where the biodegradation is very serious and the reservoir oil has been destroyed completely (Xiao et al., 2005). According to Zhang et al. (2004a), the initial reservoir space included drusy cavities and pores in limestone rather than the fractures, and the thick upper Ordovician (O_{2+3}) constructed a good preservation shield for the palaeo-reservoirs. The TD-2 well was not situated at the high position of the palaeo-structure, so the structural adjustment in Hercynian and Indosinian orogeny was moderate (Sun et al., 2003; Zhang et al., 2004a). These depositional and structural factors prevented severe biodegradation and further destruction of the reservoir oil in TD-2. Light hydrocarbon evaporation was also prevented to some extent.

Catalytic cracking of oil into gases by minerals or transition metals should be taken into account while studying the oil stability (Tannenbaum and Kaplan, 1985; Mango and Hightower, 1997; Mango and Elrod, 1998; Hill et al., 2003). Previous studies demonstrated the significant role of clay minerals like montmorillonite and illite (Espitalié et al., 1980; Tannenbaum and Kaplan, 1985). These minerals are not common in the limestone reservoir in TD-2, and the catalytic effects at clay minerals are probably not significant. We did not analyze the transition metals contents in oils and the reservoir rocks in TD-2, so the catalytic effects from transition metals could not be evaluated in this area. The catalytic effect of water in the process of oil cracking into gases has not been taken into account for the reason that the catalytic reactions may only occur near the oil–water boundary or in contacting areas. Under the circumstance of a large oil accumulation like in TD-2, the catalytic effects from water may not be significant. Nevertheless, it is worth studying in the future because the presence of water will enhance the thermal stability of oil according to the results of Price (1993, 1995) and Waples (2000).

There is no doubt that the TD-2 oil has experienced very severe thermal alteration. Previous studies have reported that plentiful pyrobitumen was found in the reservoir rocks. Polynuclear aromatic hydrocarbons were identified in TD-2 oil samples, and relatively heavy bulk carbon isotope composition was determined in TD-2 oil samples (Sun et al., 2003; Zhang et al., 2004a). All these geochemical data prove that the TD-2 oil underwent severe thermal alteration. So it is hoped that more residual oil reservoir similar to TD-2 can be expected in eastern Tarim Basin in the future. The key geological controls for occurrence of residual oil reservoir like TD-2 in eastern Tarim Basin include: (1) the high stability of the Paleozoic oil in the Tarim Basin impedes oil cracking; (2) the fast heating rate and maturation rate requires higher geological temperature and longer duration time for oil cracking; (3) the later uplift did not cause serious biodegradation; and (4) the good preservation of the palaeo-reservoirs and moderate structural adjustment. It should be emphasized that the oil-cracking gases are still important exploration targets in the eastern Tarim Basin. The natural gases and condensate in the recently discovered wells MD-1 and YN-2 of the northern slope of eastern Tarim Basin showed that oil-cracking gases were related to the palaeo-reservoirs originated from $\in$-O_1 source rocks (Zhang et al., 2004b; Sun et al., 2005; Zhao et al., 2005), which implies great potential for oil-cracking gas in this area.

6. Summary

The laboratory pyrolysis results show very high thermal stability of Paleozoic oil in Tarim Basin. The onset temperature for oil to gas cracking is about 390–400 °C. At around 650 °C, cracking at laboratory heating rates (2–20 °C/h) is completed. At geological heating rates, the onset temperature for cracking is about 148–162 °C and completion is at 245–276 °C. The kinetic parameters of oil cracking exhibited a relatively high activation energy (E_a), ranging from 58 to 76 kcal (with $A = 4.5 \times 10^{14}\ s^{-1}$). There were two types of gas precursors: one with lower E_a (<64 kcal/mol) and accounting for 64.12% of the total cracking potential, and the other with higher E_a (>67 kcal/mol) and accounts for 35.89% of the total cracking potential.

The calculated thermal cracking history of oil in TD-2 site indicated that the oil cracking started at a temperature of 165 °C ($R_o = 1.45\%$) and stopped in early Devonian (390 Ma). The degree of oil conversion in the strata of $\in$-O_1 reached 60–70% at the end of Silurian. The oil-cracking window was predicted from 165 to 258 °C at the heating rate of 3.56 °C/Ma in TD-2, which overlapped with the oil generation window (108–177 °C). Compared with the duration of oil generation windows (10 Ma, from 450 Ma to 440 Ma), the duration of the oil-cracking window was as long as 42–47 Ma (from 398–401 Ma to 438–443 Ma).

Some implications should be taken into account for the exploration of residual oil reservoirs in

eastern Tarim Basin. Firstly, laboratory results show that the Paleozoic oil in Tarim Basin has very high thermal stability and the fast heating rate requires higher geological temperature and longer duration time for oil cracking. The initial reservoir space included drusy cavities and pores in limestone, and the thick upper Ordovician (O_{2+3}) constructed a good preservation shield for the palaeo-reservoirs. The TD-2 was not situated at the high position of the palaeo-structure, so the structural adjustment in Hercynian and Indosinian orogenies was moderate. These depositional and structural factors prevent the severe biodegradation and further destruction to the reservoir oil in TD-2. Although the TD-2 oil underwent the very high thermal alteration, it might be still promising for finding more residual oil reservoirs similar to TD-2 in eastern Tarim Basin. However, the oil-cracking gases and condensates are still important exploration targets in this area.

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References

Barker, C., 1990. Calculated volume and pressure changes during thermal cracking of oil to gas in reservoirs. American Association of Petroleum Geologists Bulletin 74, 1254–1261.

Behar, F., Budzinski, H., Vandenbrouke, M., Tang, Y., 1999. Methane generation from oil cracking: kinetics of 9-methylphenanthrene cracking and comparison with other pure compounds and oil fractions. Energy and Fuels 13, 471–481.

Behar, F., Kressman, S., Rudkiewicz, J.L., Vandenbrouke, M., 1992. Experimental simulation in a confined system and kinetic modeling of kerogen and oil cracking. In: Eckardt, C.B., Maxwell, J.R., Larter, S.R., Manning, D.A.C. (Eds.), Advances in Organic Geochemistry, vol. 19, pp. 173–189.

Behar, F., Ungerer, P., Kressman, S., Rudkiewicz, J.L., 1991. Thermal evolution of crude oils in sedimentary basins: experimental simulation in a confined system and kinetic modeling. Revue de l' Institut Français du Pétrole 46, 151–181.

Behar, F., Vandenbrouke, M., Tang, Y., Marquis, F., Espitalié, J., 1997. Thermal cracking of kerogen in open and closed system: determination of kinetic parameters and stoichiometric coefficients for oil and gas generation. Organic Geochemistry 26, 321–339.

Behar, F., Vandenbrouke, M., Teerman, S.C., Hatcher, P.G., Leblond, C., Lerat, O., 1995. Experimental simulation of gas generation from coals and a marine kerogen. Chemical Geology 126, 247–260.

Bjorøy, M., Williams, J.A., Dolcater, D.L., Winters, J.C., 1988. Variation in hydrocarbon distribution in artificially matured oils. Organic Geochemistry 13, 901–913.

Boreham, C.J., Horsfield, B., Schenk, H.J., 1999. Prediction the quantities of oil and gas generated from Australian Permian coals, Bowen Basin using pyrolytic methods. Marine and Petroleum Geology 16, 165–188.

Burnham, A.K., Braun, R.L., Hugh, R.G., 1987. Comparison of methods for measuring kerogen pyrolysis rates and fitting kinetic parameters. Energy and Fuels 1, 452–458.

Burnham, A.K., Braun, R.L., Samoun, A.M., 1988. Further comparison of methods for measuring kerogen pyrolysis rates and fitting kinetic parameters. In: Mattavelli, L., Novelli, L. (Eds.), Advances in Organic Geochemistry. Pergamon Press, Oxford, pp. 839–845.

Burnham, A.K., Braun, R.L., Coburn, T.T., 1996. An appropriate kinetic model for well-preserved algal kerogens. Energy and Fuels 10, 49–59.

Burnham, A.K., Happe, J.A., 1984. On the mechanism of kerogen pyrolysis. Fuel 63, 1353–1356.

Dieckmann, V., Schenk, H.J., Horsfield, B., Welte, D.H., 1998. Kinetics of petroleum generation and cracking by programmed-temperature closed system pyrolysis of Toarcian Shales. Fuel 77, 23–31.

Dieckmann, V., Schenk, H.J., Horsfield, B., 2000. Assessing the overlap of primary and secondary reactions by closed versus open system pyrolysis of marine kerogens. Journal of Applied Pyrolysis 56, 33–46.

Dominé, F., 1989. Kinetics of hexane pyrolysis at very high pressures. 1. Experimental study. Energy and Fuels 3, 89–96.

Dominé, F., 1991. High pressure pyrolysis of *n*-hexane, 2,4-dimethylpentane and 1-phenylbutane. Is pressure and important geochemical parameter? Organic Geochemistry 17, 619–634.

Dominé, F., Dessort, D., Brevart, O., 1998. Towards a new method of geochemical kinetic modeling: implications for the stability of crude oils. Organic Geochemistry 28, 597–612.

Dominé, F., Enguehard, F., 1992. Kinetics of hexane at very high pressures—3. Application to geochemical modelling. Organic Geochemistry 18, 41–49.

Dominé, F., Marquaire, P.M., Mueller, C., Come, G.M., 1990. Kinetics of hexane pyrolysis at very high pressures. 2. Computer modeling. Energy and Fuels 4, 2–10.

Espitalié, J., Madec, M., Tissot, B., 1980. Role of mineral matrix in kerogen pyrolysis: influence on petroleum generation and migration. American Association of Petroleum Geologists Bulletin 64, 59–66.

Hayes, J.M., 1991. Stability of petroleum. Nature 352, 108–109.
Hill, R.J., Tang, Y., Kaplan, I.R., 2003. Insights into oil cracking based on laboratory experiments. Organic Geochemistry 34 (12), 1651–1672.
Horsfield, B., Schenk, H.J., Mills, N., Welte, D.H., 1992. Closed-system programmed- temperature pyrolysis for simulating the conversion of oil to gas in a deep petroleum reservoir. Organic Geochemistry 19, 191–204.
Kuo, L.-C., Michael, G.E., 1994. A multicomponent oil-cracking kinetics model for modeling preservation and composition reservoired oils. Organic Geochemistry 21, 911–925.
Liu, J., Tang, Y., 1998. An example for predicting methane generation by kerogen kinetic experiment. Chinese Science Bulletin 11, 1187–1191.
Lorant, F., Behar, F., 2002. Late generation of methane from mature kerogens. Energy and Fuels 16, 412–427.
Ma, A., Zhang, S., Zhang, D., Liang, D., Wang, F., 2005. Organic geochemistry of TD-2 oil in Tarim Basin. Xinjiang Petroleum Geology 26 (2), 148–151 (in Chinese).
Mango, F.D., 1990. The origin of light cycloalkanes in petroleum. Geochimica et Cosmochimica Acta 54, 23–27.
Mango, F.D., Elrod, L.W., 1998. The carbon isotopic composition of catalytic gas: a comparative analysis with natural gas. Geochimica et Cosmochimica Acta 63, 1097–1106.
Mango, F.D., Hightower, J., 1997. The catalytic decomposition of petroleum into natural gas. Geochimica et Cosmochimica Acta 62, 5347–5350.
McNab, J.G., Smith, P.V., Betts, R.L., 1952. The evolution of petroleum. Geochimica et Cosmochimica Acta 44, 2556–2563.
Pepper, A.S., Corvi, P.J., 1995. Simple kinetic models of petroleum formation. Part I: oil and gas generation from kerogen. Marine and Petroleum Geology 12 (3), 291–319.
Pepper, A.S., Dodd, T.A., 1995. Simple kinetic models of petroleum formation. Part II: oil–gas cracking. Marine and Petroleum Geology 12 (3), 321–340.
Price, L.C., 1981. Organic geochemistry of 300 °C, 7 km core samples, South Texas. Chemical Geology 37, 205–214.
Price, L.C., Clayton, J.L., Rumen, L.L., 1979. Organic geochemistry of a 6.9 km deep well, Hinds County, Mississippi. Gulf Coast Association and Geologic Society Transcripts 29, 352–370.
Price, L.C., Clayton, J.L., Rumen, L.L., 1981. Organic geochemistry of the 9.6 km Bertha Rogers #1, Oklahoma. Organic Geochemistry 3, 59–77.
Price, L.C., 1993. Thermal stability of hydrocarbons in nature: limits, evidence, characteristics, and possible controls. Geochimica et Cosmochimica Acta 57 (14), 3261–3280.
Price, L.C., 1995. Origins, characteristics, controls, and economic viabilities of deep-basin gas resources. Chemical Geology 126 (3–4), 335–349.
Schenk, H.J., di Primo, R., Horsfield, B., 1997. The conversion of oil into gas in petroleum reservoirs. Part 1: comparative kinetic investigation of gas generation from crude oils of lacustrine, marine and fluviodeltaic origin by programmed temperature closed-system pyrolysis. Organic Geochemistry 26, 467–481.
Schenk, H.J., Horsfield, B., 1993. Kinetics of petroleum generation by programmed-temperature closed-system versus open-system pyrolysis. Geochimica et Cosmochimica Acta 57, 623–630.
Simoneit, B.R.T., Fetzer, J.C., 1996. High molecular weight polycyclic aromatic hydrocarbons in hydrothermal petroleums from the Gulf of California and Northeast Pacific Ocean. Organic Geochemistry 24 (10/11), 1065–1077.
Sun, L., Zhou, X., Wang, G., 2005. Contributions of petroleum geology and main directions of oil and gas exploration in the Tarim Basin. Chinese Journal of Geology 40 (2), 167–178.
Sun, Y., Jin, Y., Gu, Q., Shen, Y., Yang, F., 2003. Timing of paleo-oil accumulation in Tadong No. 2 Well, Tarim Basin. Petroleum Exploration and Development 30 (5), 31–33 (in Chinese).
Sweeney, J.J., Burnham, A.K., 1990. Evaluating of a simple model of vitrinite reflectance based on chemical kinetics. American Association Petroleum Geologists Bulletin 74 (10), 1559–1570.
Tang, Y., Stauffe, M., 1994. Multiple cold trap pyrolysis gas chromatography: a new technique for modeling hydrocarbon generation. Organic Geochemistry 22 (3–5), 863–872.
Tang, Y., Stauffe, M., 1995. Formation of pristene, pristane and phytane: kinetic study by laboratory pyrolysis of Monterey source rock. Organic Geochemistry 23 (5), 451–460.
Tang, Y., Jenden, P.D., Teerman, S.C., 1991. Thermogenic methane formation in low-rank coals-published models and results from laboratory pyrolysis of lignite. In: Manning, D. (Ed.), Proceedings of the 15th Meeting of European Association of Organic Geochemistry. Manchester University Press, Manchester, UK, pp. 329–331.
Tannenbaum, E., Kaplan, I.R., 1985. Low-Mr hydrocarbons generated during hydrous and dry pyrolysis of kerogen. Nature 317, 708–709.
Tsuzuki, N., Takeda, N., Suzuki, M., Yokoi, K., 1999. The kinetic modeling of oil cracking by hydrothermal pyrolysis experiments. International Journal of Coal Geology 39, 227–250.
Ungerer, P., Behar, F., Villalba, M., Heum, O.R., Audibert, A., 1988. Kinetic modelling of oil cracking. Organic Geochemistry 13, 857–868.
Ungerer, P., 1990. State of the art in kinetic modeling of oil formation and expulsion. Organic Geochemistry 16, 1–25.
Waples, D.W., 2000. The kinetics of in-reservoir oil destruction and gas formation: constraints from experimental and empirical data, and from thermodynamics. Organic Geochemistry 31 (6), 553–575.
Xiao, Z., Lu, Y., Sang, H., Pan, Z., Li, Y., 2005. A typical Cambrian oil reservoir: origin of oil reservoir in Well TZ62, Tarim Basin. Geochimica 34 (2), 155–160 (in Chinese).
Xiong, Y., Geng, A., Wang, Y., Liu, D., Jia, R., Shen, J., et al., 2001. Kinetic simulating experiment on the secondary hydrocarbon generation of kerogen. Science in China, Series D 45, 13–20.
Zhang, S., Wang, Z., Wang, F., Liang, D., Xiao, Z., Huang, H., 2004a. Oil accumulation history in Tadong 2 reservoir in Tarim Basin, NW China—a case study of oil stability and cracking. Petroleum Exploration and Development 31 (6), 25–31 (in Chinese).
Zhang, S., Zhao, W., Wang, F., Cheng, J., Xiao, Z., Zhong, N., et al., 2004b. Paleozoic oil cracking gas accumulation history from eastern part of the Tarim Basin—a case study of the YN2 gas reservoir. Natural Gas Geoscience 15 (5), 441–451 (in Chinese).

Zhang, B., Zhao, M., Xiao, Z., 2000a. Characteristics of premium gas source rocks in Tarim Basin. Xinjiang Petroleum Geology 1, 33–37 (in Chinese).

Zhang, Y., Jin, Z., Liu, G., Li, J., 2000b. Study on the formation of unconformities and the amount of eroded sedimentations in Tarim Basin. Earth Science Frontiers 7 (4), 449–457 (in Chinese).

Zhao, M., Zhang, S., Liao, Z., 2001. The cracking gas from crude oil and its significance in gas exploration. Petroleum Exploration and Development 4, 47–49 (in Chinese).

Zhao, W., Zhang, S., Wang, F., Chen, J., Xiao, Z., Song, F., 2005. Gas accumulation from oil cracking in the eastern Tarim Basin: a case study of the YN2 gas field. Organic Geochemistry 36 (12), 1602–1616.