Gas sources of the YN2 gas pool in the Tarim Basin—Evidence from gas generation and methane carbon isotope fractionation kinetics of source rocks and crude oils

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Abstract

The YN2 gas pool in the eastern Tarim basin has been believed to be an accumulation of gases resulting from oil-cracking. However, this gas source model cannot explain such geochemical characteristics of the natural gases as heavier carbon isotope values ($\delta^{13}C_1 = -37.5‰$ to $-36.2‰$; $\delta^{13}C_2 = -34.7‰$ to $-30.9‰$) and high content of nitrogen gas (15.5% on average). In this study, we performed pyrolysis experiments on typical source rock and crude oil samples selected from the basin, evaluated their kinetic parameters of gas generation and methane carbon isotopic fractionation, and extrapolated them to geological conditions. The results show that neither kerogen-cracking gas nor oil-cracking gas can act as the single gas source of the YN2 gas pool. By contrast, a mixing model of 55% kerogen-cracking gas and 45% oil-cracking gas results in an excellent match with the geochemical characteristics of the gas pool. The gas condensate from the YN2 gas pool originated from the cracking of oils in mid-upper Ordovician strata, and the nitrogen gas was mainly derived from the cracking of kerogen in Cambrian–lower Ordovician mudstones in the Yingjisu depression center during the very high level of maturation. The YN2 gas pool went through three stages of formation: (1) oils from Cambrian–lower Ordovician source rocks accumulated in Cambrian and Ordovician reservoirs during the middle Ordovician, and gases were generated from both kerogen and paleo-oil pools in the Cambrian–lower Ordovician strata during late Ordovician to early Devonian; (2) gases leaked during either late Devonian to Triassic due to uplifting, or late Jurassic due to intense faulting activity in this area; (3) gases were regenerated from the late cracking of kerogen in the Cambrian–lower Ordovician strata as well as from oil-cracking in mid-upper Ordovician reservoirs with rapid subsidence after the Cretaceous. The two types of gas mixed and accumulated in the Jurassic traps to form the present wet gas pool with high nitrogen content and a heavier methane carbon isotopic value.
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Keywords: Tarim basin; YN2 gas pool; Natural gas source; Methane carbon isotope; Kinetic modeling

1. Introduction

The YN2 gas pool, located in the Yingjisu depression, has been regarded as the biggest discovery in the eastern area of the Tarim Basin (Wang et al., 2003). Its prognostic natural gas and condensate reserves are estimated to be $1042.5 \times 10^8\,m^3$ and $532.7 \times 10^4\,t$, respectively. The gas source of the pool has attracted the attention of many geochemists and geologists (Wang et al., 2003; Zhang et al., 2004a; Zhao et al., 2005; Xiao and Li, 2005; Huang et al., 2005). At present, the natural gas of the YN2 gas pool is widely believed to have originated from the cracking of oil in paleo-oil pools in Cambrian–Ordovician reservoirs (Wang et al., 2003; Zhang et al., 2004a; Zhao et al., 2005; Xiao et al., 2005). The first of two major lines of evidence is the relatively high content of heavy gaseous hydrocarbons (C_{2+}), with an average dryness index of 0.89 (defined as the ratio of C_1/C_1–C_5 by volume). The Cambrian and lower Ordovician source rocks in the studied area, however,

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matured to reach the dry gas stage during the gas pool formation period and it was therefore impossible for them to provide such wet gases (Zhao et al., 2005). The second line of evidence is derived from the geological background of the gas pool. The early Paleozoic sediments in the Yingjisu depression are as thick as 7000 m and the paleo-oil pools within these strata have been heated to a temperature of more than 190 °C, high enough to initiate the transformation of oil to gas at the heating rate of the Tarim basin (Waples, 2000; Zhang et al., 2004a). However, this gas source model cannot explain the following geochemical characteristics of the gas pool:

(1) *High content of nitrogen gas*: The content of nitrogen gas in the YN2 gas pool is as high as 17.87% and the ratio of nitrogen gas to methane by volume is up to 0.26, whereas the ratio of nitrogen to methane is generally less than 0.1 in pyrolysis products from experiments on marine oils from the Tarim basin (Li et al., 2003).
(2) *Heavy carbon isotopes of natural gases*: The carbon isotopes of methane and ethane are, respectively, $\delta^{13}C_1 = -37.5‰$ to $-36.2‰$ and $\delta^{13}C_2 = -34.7‰$ to $-30.9‰$, heavier than those values for the Anadarko gas in Kansas reported by Jenden et al. (1988), believed to be an oil-cracking gas accumulation (Prinzhofer and Hu, 1995). According to the geological model of methane carbon isotopic fractionation calculated by Tang et al. (2000) for a n-C_{18} alkane sample with a carbon isotopic composition of $-30.3‰$, the cumulative and instantaneous methane carbon isotopic composition of its cracked gas are lighter than $-50‰$ and $-45‰$, respectively, at a temperature of around 190 °C. This temperature corresponds to an oil cracking extent of at least 60% according to the results of Waples (2000). Using diamondoid hydrocarbons as the indicator of oil destruction, Zhao et al. (2005) believed the gas condensate associated with the natural gases in the YN2 gas pool corresponds to oils with 60–70% thermal cracking. In other words, the carbon isotopic composition of methane in the YN2 gas pool should be similar to the results of Tang et al. (2000) if the methane is uniquely from the cracking of oil that has a similar carbon isotopic composition as the n-C_{18} alkane sample. As a matter of fact, the Tarim marine oil has a more negative isotopic value than the n-C_{18} alkane, the carbon isotope values of the Tarim oil cracked gas are expected to be lighter.

The disagreements between isotopic values and dryness index of the YN2 natural gases imply the possibility that the gases have a mixed origin from different gas sources. In recent years, kinetic methods of modeling gas generation and methane carbon isotopic fractionation have been successfully applied to investigate natural gas origin and accumulation (Cramer et al., 1998, 2001; Tang et al., 2000; Cramer, 2004; Xiong et al., 2004; Zou et al., 2005; Xiao

et al., 2006). In the present study, we have established geological models of gas generation and methane carbon isotopic fractionation in the studied area using kinetic methods based on typical kerogen and crude oil pyrolysis data in order to reevaluate the origin of natural gases in the YN2 gas pool.

2. Geological setting

The Yingjisu area is situated in the eastern part of the Tarim Basin (Fig. 1). It was the eastern stretch slope of the Manjiaer Depression till early Devonian, then it was uplifted and eroded from late Devonian to Triassic. This area subsided again from the Jurassic and accumulated nearly 3000 m of late Mesozoic and Cenozoic sediments to form a separate depression, the Yingjisu Depression (Jia, 1999; Wu et al., 2002; Zhao et al., 2005; Fig. 2). The YN2 gas pool is located at the top of the YN2 trap structure. The burial history of the well YN2 is presented in Fig. 3.

Briefly, the structural evolution of the Yingjisu area can be divided into three stages (Jia, 1999; Wu et al., 2002):

(1) *Rapid subsidence during the Cambrian–Silurian*: Some 7000 m of thick marine sediments developed and the YN2 trap structure began to form with the faulting activity during this period.
(2) *Uplift and erosion from late Devonian to Triassic*: Due to the Hercynian and the following Indosinian Movements, this area was uplifted and the lower Paleozoic strata were eroded. The total erosional thickness of Silurian to Devonian strata has been estimated to be around 1000 m (Zhang et al., 2004a).
(3) *Re-subsidence after Triassic*: About 3000 m thickness of non-marine sediments formed during this period, secondary faults began to develop near the YN2 trap structure and the YN2 trap structure was ultimately formed by the end of Cretaceous time (Wang et al., 2003).

In the Yingjisu Depression, a few sets of dark mudstones in the Cambrian and lower Ordovician strata are the major source rocks (Zhang et al., 2004a, b; Xiao et al., 2005; Zhao et al., 2005). The dark mudstone samples taken from well TD1 are characterized by a high TOC content (2.28–3.07%) and a very high maturation level of over 2.5% equivalent vitrinite reflectance (Xiao et al., 2005). The lower Jurassic sandstones are the major gas production layer, the overlying tightly cemented sandstones act as direct caps, and lower Cretaceous mudstones are the regional caps in the YN2 gas pool area (Wang et al., 2003).

3. Pyrolysis experiments and determination of kinetic parameters

3.1. Samples

Two samples from the Tarim Basin were used in the study. A crude oil is from the Triassic sandstone reservoir
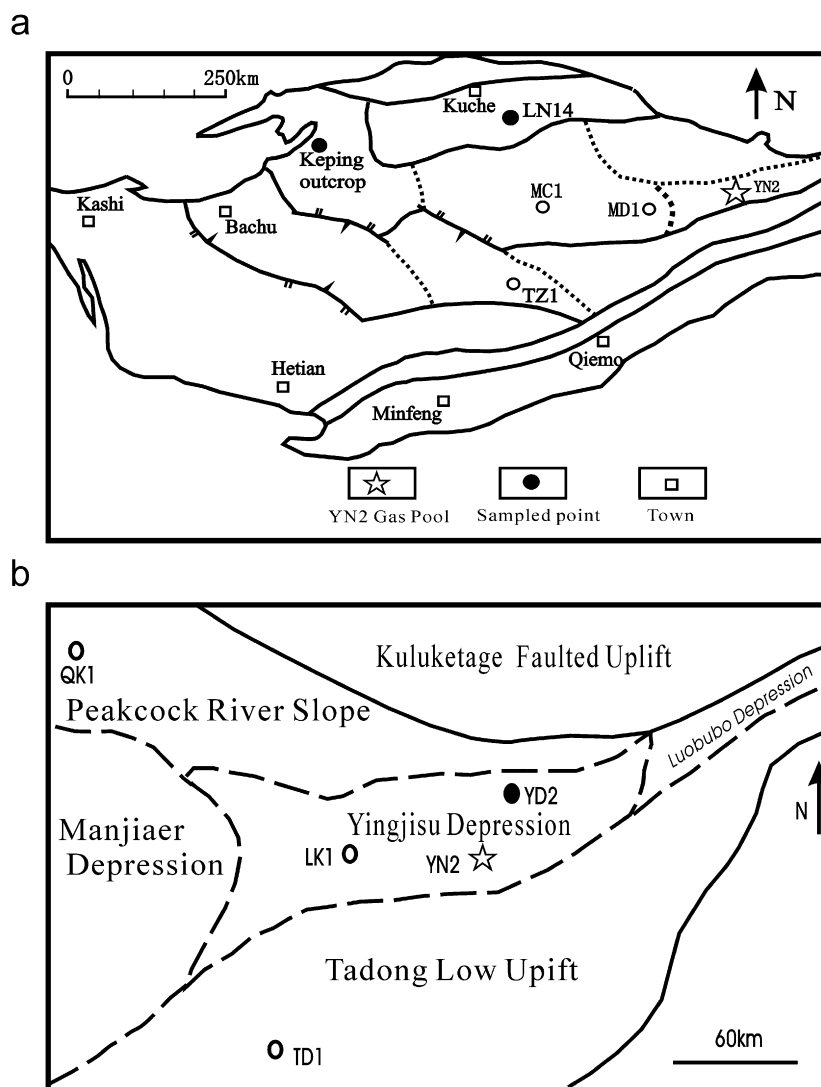
a

b

Fig. 1. Maps showing locations of samples and YN2 gas pool (a) and adjacent structures of the Yingjisu Depression (b) (modified from Liu et al., 2004).

of the well LN14 at a depth of 4609–4625 m. The oil is believed to be of marine origin and derived from Cambrian–Ordovician source rocks (Zhang et al., 2004b). It is normal oil with a density of 0.8397 g/cm³ at 20 °C and a sulfur content of 0.3%. The other sample is an Ordovician mudstone from the Keping outcrop. It is rich in organic matter, with a TOC content of 2.6%, and a relatively high maturation level with EqVRo = 1.10%. The Rock-Eval analysis showed a T_{max} of 457 °C and a hydrogen index of 121.1 mg/TOC, indicating a post-oil thermal stage but still high potential of gas generation. This high maturity sample was selected for the pyrolysis experiment because our aim was to investigate the secondary gas generation in the study area that has experienced a rapid burial leading to the end of oil generation from Cambrian and lower Ordovician source rocks before the severe late Devonian uplift. As studied by Behar et al. (1995), the pyrolysis of immature type II kerogen samples in a confined system yields gases that mainly originate from the secondary cracking of early

generated oils. So the relatively highly matured sample was selected in order to reduce this influence as much as possible. According to the procedures suggested by Alpern (1980), kerogen was separated from this mudstone sample. The geological and geochemical characteristics of the oil and kerogen samples are presented in Table 1.

3.2. Pyrolysis experiment

The pyrolysis experiments were conducted in sealed gold tubes (Liu and Tang, 1998; Hill et al., 2003; Xiao et al., 2005b) at temperatures from 200 to 620 °C. Different from the MSSV experiments that usually choose three fast heating rates (Horsfield et al., 1992; Schenk and Horsfield, 1998; Schenk et al., 1997), the present experiment uses two slow heating rates of 2 and 20 °C/h as previous authors did (Tang et al., 1996; Xiong et al., 2004; Zou et al., 2005). This is because the kinetic parameters derived from experiments with low heating rates are more reasonable when extrapolating to geological conditions (Schenk and Dieckmann,

Stratigraphy	Thickness (m)	Lithologic sucession	Lithology description	Source	Reservoir	Cap rock	Tectonic evolution
Quaternary	26-35		Mmudstone and siltstone				
Upper Tertiary	1138-1195		Mudstone and siltstone				Faulted and depredded basin
Lower Tertiary	315~556		Sandstone and siltstone				
Cretaceous	180~1060		Upper coarse sandstone				
			middle mudstone			▒	
			lower sandstone and siltstone				
Jurassic	800~1000		Upper mudstone and coals with thin sandstones	▒		▒	
			Middle sandstones and siltstones with thin sandy mudstones			▒	
			Lower sandstones and conglomerates		▒		
Silurian	436~783		Sandstones with conglomerates		▒		Continental margin rifted basin
Middle-upper Ordovician	4000~5000		Sandstones and siltstones		▒		
Cambrian and lower Ordovician	400~600		Mudstone and muddy limestones	▒			

Fig. 2. Simplified stratigraphic column in the Yingjisu area (modified from Wang et al., 2003).

2004). A constant confining pressure of 50 MPa was used during the whole pyrolysis experiment with an error of less than 2 MPa.

The gaseous hydrocarbons (C_{1-5}) were analyzed by an HP 5890 II gas chromatograph instrument and quantified using the outer mark method. The GC conditions were Poraplot Q capillary column ($30\,m \times 0.25\,mm \times 0.25\,\mu m$) and helium carrier gas. The gas was injected at a temperature of $50\,°C$, held for 2 min, and then the oven was subsequently heated to $180\,°C$ at a rate of $4\,°C/min$ and held at $180\,°C$ for 15 min.

The methane carbon isotopic composition was measured on a Delta plus XL GC-IRMS. At least two measurements were performed for each gas sample to confirm the errors were less than ± 0.3 (‰, PDB). A Poraplot Q capillary column ($30\,m \times 0.32\,mm \times 0.25\,\mu m$) was used in the GC, with helium as carrier gas. The GC-MS conditions were

injection temperature $50\,°C$ (held for 3 min), head pressure of $58.6\,KPa$, programmed heating from 50 to $150\,°C$ at a rate of $4\,°C/min$, and then held at $150\,°C$ for 8 min.

3.3. Determination of kinetic parameters

Based on the pyrolysis data from the kerogen and crude oil samples at two different heating rates, the gas generation kinetic parameters were evaluated by the software Kinetics 2000 developed by Braun and Burnham (1998). The kinetic parameters of methane carbon isotopic fractionation are fitted by the method of Tang et al. (2000) using the GOR-isotope software (version 1.48, Geoiso-Chem Corporation, 2003). We used a fixed frequency factor and a smooth activation energy distribution to avoid the artificial isotopic oscillation derived from the discrete activation energy distribution (Tang et al., 2000). In
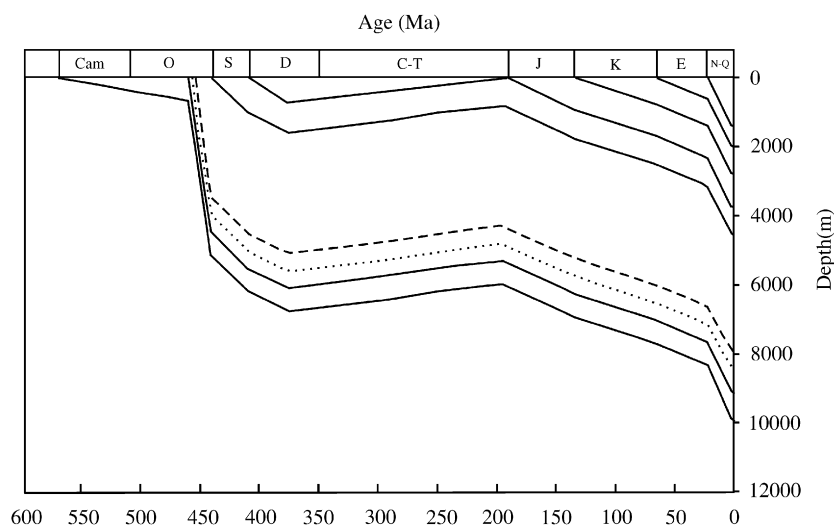
Fig. 3. Plot showing the burial history of well YN2. The dotted and dashed lines represent the burial history of paleo-oil pools in mid-upper Ordovician strata, respectively, 500 and 1000 m from the top of lower Ordovician strata as suggested by Xiao and Li (2005). The stratigraphic data from Silurian to Quaternary are taken from the Tarim oil field, the latest version in 2005 and the data on the Cambrian-Ordovician strata are provided by Huang et al. (2005). The erosion thickness during late Devonian to Triassic uplifting is estimated by Zhang et al. (2004a).

Table 1
Geochemical characteristics of kerogen and crude oil samples selected for pyrolysis experiment

No.	Type	Age	Characteristics[a]								
			Ro (%)	T_{max} (°C)	TOC (%)	S2 (mg/kerogen)	HI (mg/TOC)	VLM (%)	M(Aor) (%)	B (%)	$\delta^{13}C$ (‰)
SA	Kerogen	O	1.1	457	57.4	69.5	121.1	5–10	85–90	2–5	−30.46
				Density (g/cm³)		Wax content (%)		Sulfur content (%)		Viscosity (mPa s)	$\delta^{13}C$ (‰)
LN	Crude oil	T		0.8397(20 °C)		4.43		0.3		4.18(50°C)	−32.1

[a]VLM—vitrinite like macerals; M(Aor)—micronite (amorphous macerals); B—bitumen.

contrast to the kerogen-cracking gas, the oil-cracking gas is characterized by a high content of C_{2-5} heavy gases and a strong secondary cracking at high thermal stress in a closed system (Hill et al., 2003). The completion of oil cracking can not be represented by the maximum methane yield, but rather the total gas yield (Schenk et al., 1997). So, the C_{1-5} gas generation kinetic parameters for oil cracking and the methane generation and carbon isotope fractionation kinetic parameters for both samples were determined in this study. The results are presented in Figs. 4 and 5 and Table 2.

The mean activation energy for the C_{1-5} generation is 59.7 kcal/mol for the oil sample, which is similar to the results reported by Waples (2000). The mean activation energies of methane generation for the oil and kerogen samples were calculated to be 63–64 kcal/mol, which is higher than those determined in open systems due to the secondary cracking of C_{2-5} heavy gases and complex aromatization/polycondensation reactions at higher thermal stress in a closed system (Hill et al., 2003; Dieckmann et al., 2006). As to the methane carbon isotopic fractionation parameters, the lowest and highest activation energy

differences for the oil and kerogen samples are also quite different indicating different methane precursors for the two samples, for example, the different contribution of C_{2-5} cracking to methane generation. Moreover, the initial carbon isotopic composition for the oil-cracking methane is more negative than that for the kerogen-cracking methane. This can be explained by the carbon isotopic fractionation during the transformation from kerogen to oil (Clayton, 1991).

4. Paleo-geothermal model

The geological parameters needed for the establishment of a geologically specific model of gas generation and methane carbon isotopic fractionation include burial history, paleo-geothermal gradients and paleo-surface temperatures. The burial history has been discussed in Section 2, and the paleo-surface temperature for the Tarim Basin is assumed to be 20 °C on average (Jin, 1997; Wang and Zhang, 2003; Wang et al., 2004). The following discussion will be focused on the paleo-geothermal gradients.
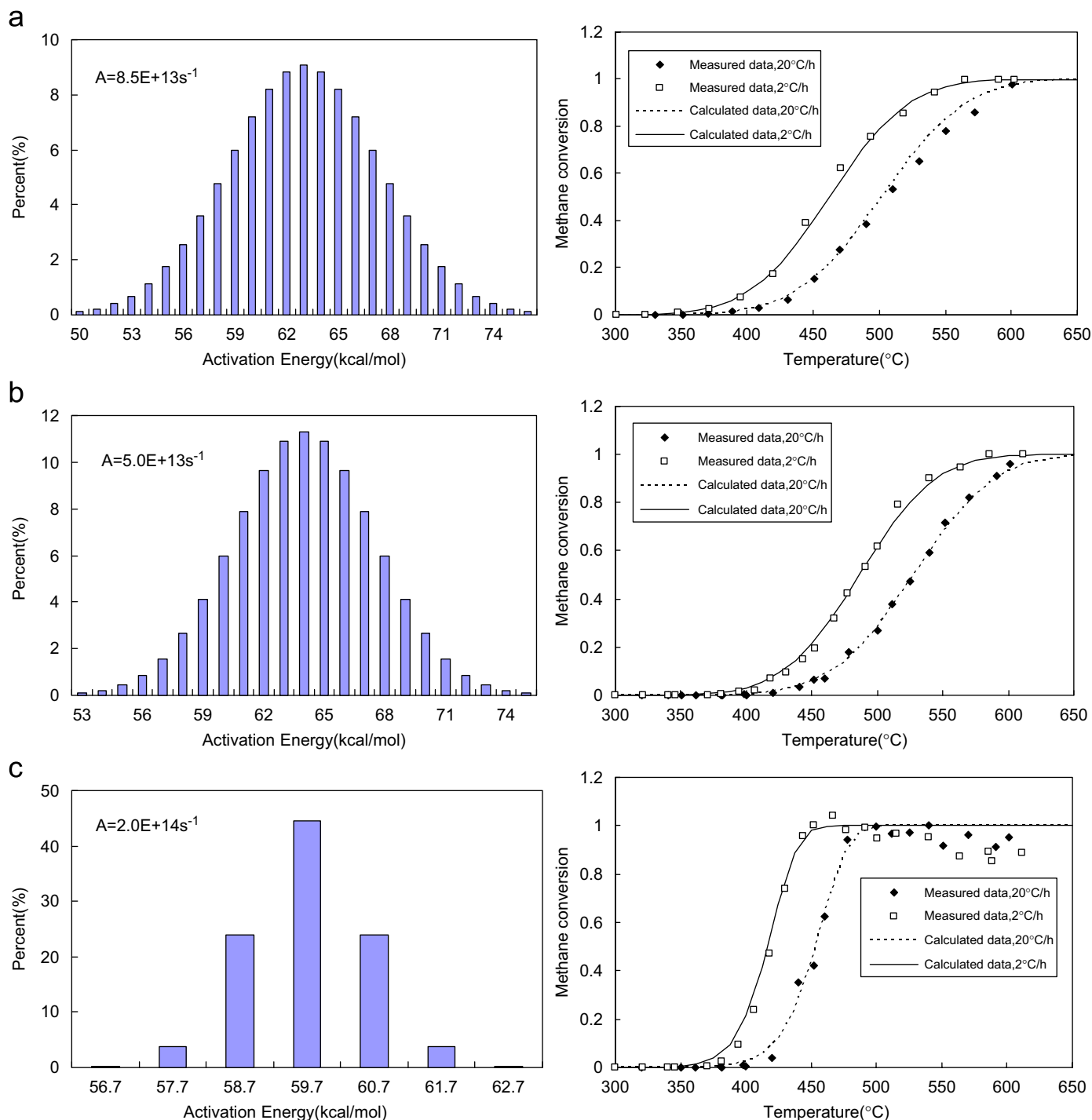
Fig. 4. The activation energy distributions and frequent factors of gas generation (left), and corresponding comparison of calculated gas conversion with measured results (right) for the two studied Tarim samples based on the sealed gold tube pyrolysis data at two different heating rates. The software Kinetics 2000 was used. See details in text. (a) Methane from kerogen sample, (b) methane from crude oil sample; (c) C_{1-5} gases from crude oil sample.

Some work has been done recently on the paleo-geothermal gradients of the Tarim Basin and a consensus has emerged that the geothermal gradients decreased with the passing of geological time (Liang and Zhang, 2001; Wang et al., 2004; Zhao et al., 2005). Wang et al. (2004) modeled the paleo-geothermal gradients in the Mesozoic-

Cenozoic based on measured vitrinite reflectance data from the Yingjisu Depression. However, no Paleozoic paleo-geothermal gradient data is currently available because of the absence of maturation data from Paleozoic strata in this area. Fortunately, we have obtained two Cambrian–Ordovician rock samples containing abundant solid
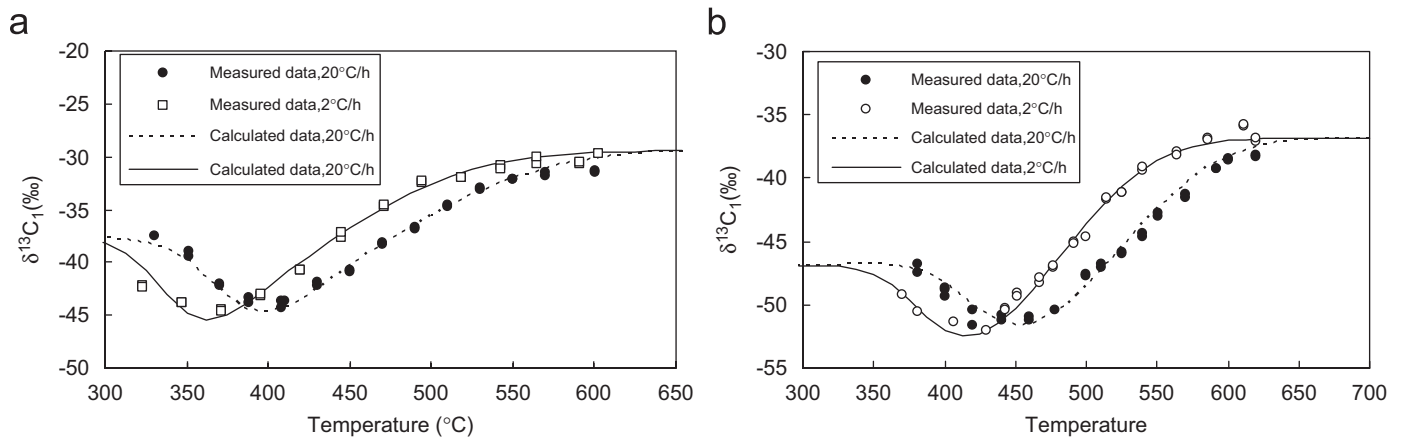
a

b

Fig. 5. The fitting of carbon isotopic fractionation of methane generated by sealed gold tube pyrolysis of the studied kerogen (a) and crude oil (b) samples. The fitted parameters are presented in Table 2.

Table 2
Kinetic parameters of methane carbon isotope fractionation for studied kerogen and crude oil samples

Samples	Methane carbon isotope fractionation kinetic parameters[a]					
	α	β_L (cal/mol)	β_H (cal/mol)	μ (cal/mol)	σ (%μ)	δ_{init} (‰)
Kerogen	1.015	0.58	56.16	52,000	4	−30.257
Crude oil	1.02	−12.58	75.16	55,000	7	−36.843

[a] α—the ratio value of $^{13}A/^{12}A$; β_L—the lowest activation energy difference; β_H—the highest activation energy difference; μ—the mean activation energy of Sigmoid function; σ—the variance of Sigmoid function; δ_{init}—the initial carbon isotope of methane precursor (Tang et al., 2000).

bitumen from the well YD2 at depths of 4414 m (Ordovician) and 4754 m (Cambrian). This well is close to the well YN2 (Fig. 1b) and the thermal maturation of the Cambrian–Ordovician strata mainly occurred before late Devonian due to subsequent uplift. Thus, the bitumen reflectance values are in fact an indicator of the thermal history of its host rock during the early Paleozoic. The measured bitumen random reflectance value is 1.48% for the Ordovician sample and 1.70% for the Cambrian sample, with equivalent vitrinite reflectances of 1.32% and 1.46% respectively, using the formula of VRo = 0.66-BRo + 0.34 (Liu and Shi, 1994) where Bro is measured bitumen random reflectance (%). We simulated the thermal history of the well YD2 using the modified Easy%Ro method (Tang et al., 1996) and found that the calculated Ro has a good match with the measured Ro when the geothermal gradient model listed in Table 3 was used. Compared with the high geothermal gradients of 3.2–3.8 °C/100 m in the Tadong Uplift (Wang and Zhang, 2003), the Paleozoic geothermal gradients from this modeling are relatively low and quite similar to the gradients of the well QK1 in the Peacock River slope, northwest Yingjisu Depression (Liang and Zhang, 2001; Fig. 1b). This indicates that the maturities of early Paleozoic source rocks in the Yingjisu Depression were overestimated by Zhang et al. (2004a) and Zhao et al. (2005) by using the geothermal gradients from the Tadong Uplift.

5. Geochemical models of gas generation and methane carbon isotopic fractionation

5.1. Kerogen-cracking gas

As mentioned above, the Cambrian and lower Ordovician marine mudstones are the major gas source rocks in the Yingjisu Depression (Wang et al., 2003; Zhang et al., 2004a; Zhao et al., 2005). As the gas migrated dominantly in an upward direction, the well YN2 was selected as the simulation site to establish the gas generation and methane carbon isotopic fractionation history for the source rocks. Fig. 6 presents the results from the target source rocks. Two stages of gas generation are obvious. The first stage covers the early Paleozoic with a methane conversion of 0.48–0.65 at the end of the Devonian. Following the uplift of this area during the Carboniferous-Triassic, the thermal maturation of the source rocks ceased. The second stage began from the late Mesozoic, the source rocks re-generated gas and the methane conversion increased by 0.1–0.15. The gas has a cumulative methane carbon isotopic composition of −34.8‰ to −31.8‰ and an instantaneous value of −25.9‰ to −21.5‰ at present.

5.2. Oil-cracking gas

Previous studies have indicated that the paleo-oil pools not only developed in Cambrian and lower Ordovician

reservoirs, but also in mid-upper Ordovician clastic reservoirs (Zhang et al., 2003; Wang et al., 2003; Nie et al., 2005). Xiao and Li (2005) inferred that the paleo-oil pools in the mid-upper Ordovician strata were distributed in the lower part of these strata, with the shallowest about 1000 m away from the top of lower Ordovician (Fig. 3) based on the oil generation history. Fig. 7 presents the results of gas generation and methane carbon isotopic

Table 3
Modeled geothermal gradient sequence for well YD2 in Yingjisu Depression

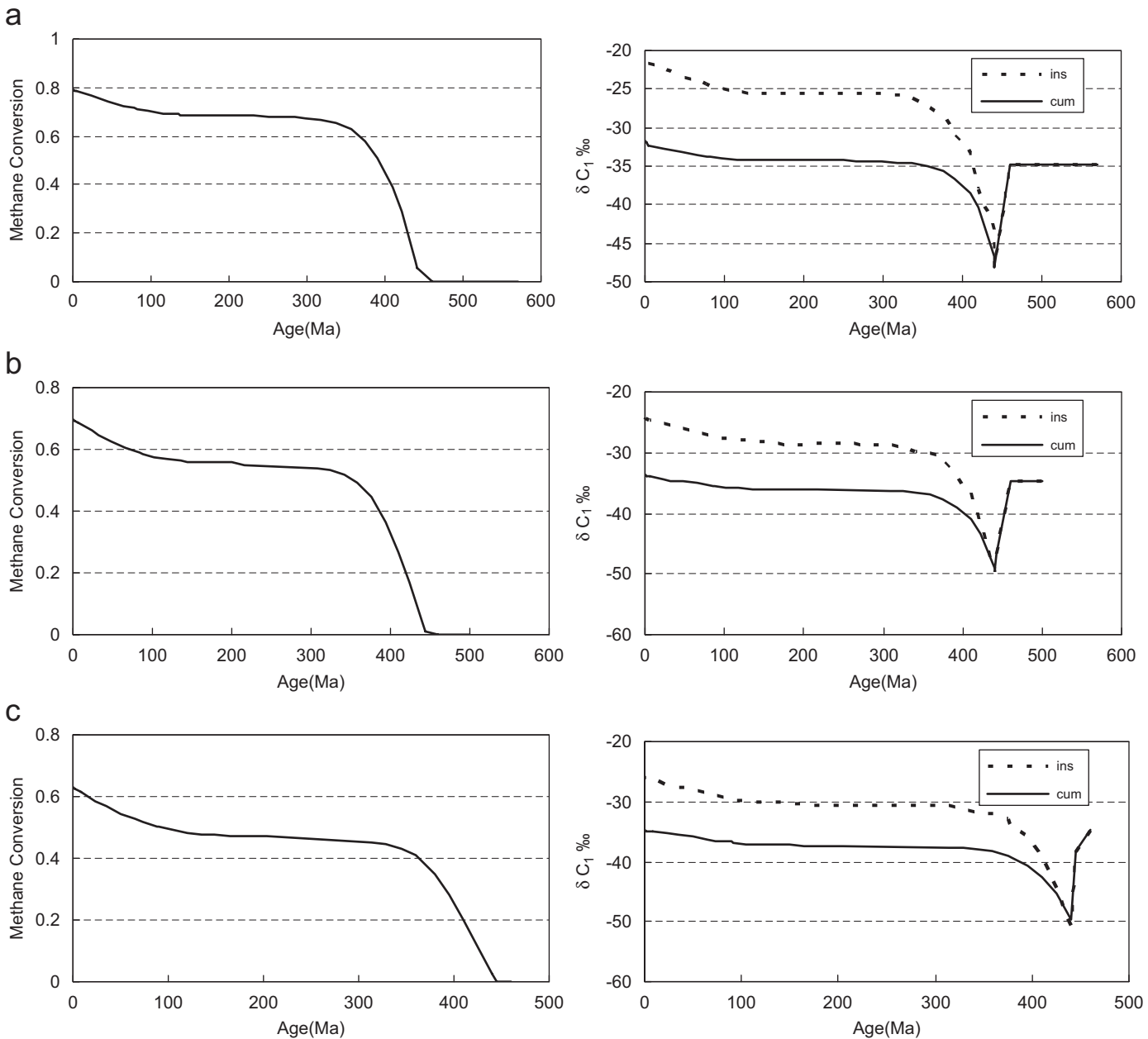| Period	Cam	O	S	D–P	T	J	K	E	N–Q
Geothermal gradient (°C/100 m)	3.0	3.0	2.9	2.8	2.7	2.6	2.5	2.4	2.1

Fig. 6. Geological models of methane generation (left) and methane carbon isotopic fractionation (right) for source rocks from well YN2 at three representative sites using the kinetic parameters for kerogen cracking from this paper. (a) Cambrian bottom, (b) lower Ordovician bottom and (c) lower Ordovician top. The instantaneous methane carbon isotopic composition at 65 Ma is −24.1‰, −26.6‰ and −28.7‰, respectively, for sites a, b and c.
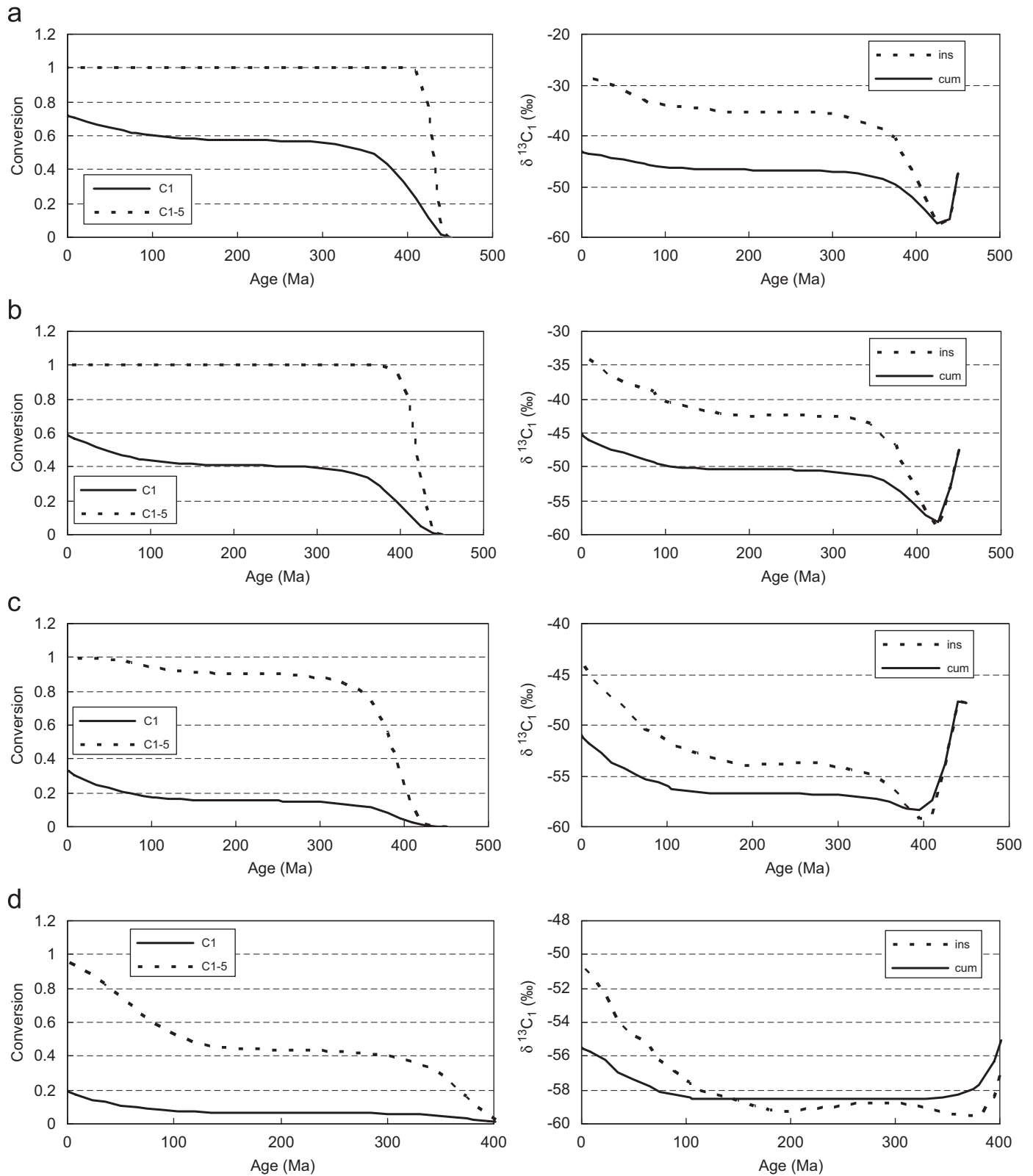
Fig. 7. Geological models of gas generation (left) and methane carbon isotopic fractionation (right) for paelo-oil pools in Cambrian–Ordovician strata from well YN2 using the kinetic parameters for oil cracking from this paper. (a) Oils at Cambrian bottom, (b) oils at lower Ordovician bottom, (c) and (d) oils in mid-upper Ordovician strata, 500 and 1000 m from the lower Ordovician top. The instantaneous methane carbon isotopic composition at 65 Ma is −49.5‰ and −55.4‰, respectively, for sites c and d. Gases from oil cracking at sites A and B are not considered. See details in text.

fractionation of the oil-cracking gas in the Cambrian and Ordovician reservoirs. It is clear that the oil in the Cambrian–lower Ordovician reservoirs had been totally transformed into gases by the end of the Devonian. The long period uplifting, however, would lead to the loss of most of these gases before the Jurassic trap structures were formed. By contrast, oil pools in the mid-upper Ordovician reservoirs had a lower C_{1-5} conversion of 0.4–0.8 before the uplift, and the residual oil pools could be re-cracked into gas during the rapid Mesozoic and Cenozoic subsidence. After the Cretaceous, the C_{1-5} conversion of the oil-cracking gases from mid-upper Ordovician reservoirs has had an increase of 0.2–0.6 and this could provide abundant gases. The cumulative and instantaneous methane carbon isotopic composition of the oil-cracking gases in mid-upper Ordovician reservoirs are, respectively, −55.5‰ to −51.0‰ and −50.5‰ to −43.8‰ at present.

6. Discussion

6.1. Sources of the YN2 gas pool

Two aspects should be considered when the kinetic models of gas generation and methane carbon isotopic fractionation are applied to constrain the source of a gas pool. One is that the calculated methane carbon isotopic value from the assumed gas source can match that of the field gas, and the other is that the assumed gas source can produce enough gases, in terms of C_{1-5} or C_1 conversion increase during the formation period of the gas pool. The YN2 gas has a methane carbon isotopic value of −36.2‰ to −37.5‰, the trap structure formed in the late Cretaceous and the effective gas accumulation began after 65 Ma (Wang et al., 2003; Zhang et al., 2004a). According to this information, it can be concluded that neither kerogen-cracking gases nor oil-cracking gases can act as a unique gas source for the YN2 gas pool since the respective kerogen-cracking methane carbon isotopes (Fig. 6) and oil-cracking methane carbon isotopes (Fig. 7) are, respectively,

much heavier and lighter than the field methane gas, though both sources have had a significant methane increase after 65 Ma. Thus, the mixing model for the two types of gases is believed to provide the best explanation for the methane carbon isotopic composition of the natural gases from the YN2 gas pool.

The end-member method of determining the methane carbon isotopic value (Johnson et al., 1993; Gurgey et al., 2005) was used to estimate the percentages of gases of both origins in the YN2 gas pool. The bottom of the lower Ordovician was selected as the representative source rock modeling point, and a point within the mid-upper strata, 1000 m from the top of lower Ordovician (see Section 5.2) as the site of the mid-upper Ordovician paleo-pool, giving the end-member methane carbon isotope values of −25.3‰ and −52.4‰, respectively (Fig. 8). Thus, the percentage of the two kind gases can be estimated by the equations:

$$X + Y = 100\%, \tag{1}$$

$$-52.4‰X − 25.3‰Y = −37.5‰, \tag{2}$$

where X and Y are the percentages of oil-cracking gas and kerogen-cracking gas, respectively; and −37.5‰ is the original and unaltered methane carbon isotopic value of the YN2 gas pool (Huang et al., 2005). The two equations give $X = 45\%$ and $Y = 55\%$, i.e., the YN2 gas pool has an estimated 45% of oil-cracking gas and 55% of kerogen-cracking gas.

6.2. Source of gas condensate

According to the oil-cracking modeling results, the paleo-oil pools in the Cambrian–lower Ordovician strata were completely transformed into gases in the late Devonian, so there is no possibility that the gas condensate from the YN2 gas pool was derived from these paleo-oil pools. However, the paleo-oil pools in mid-upper Ordovician strata had a lower extent of cracking and have not now been completely transformed to gases. The extent of oil-cracking from the top of the mid-upper Ordovician
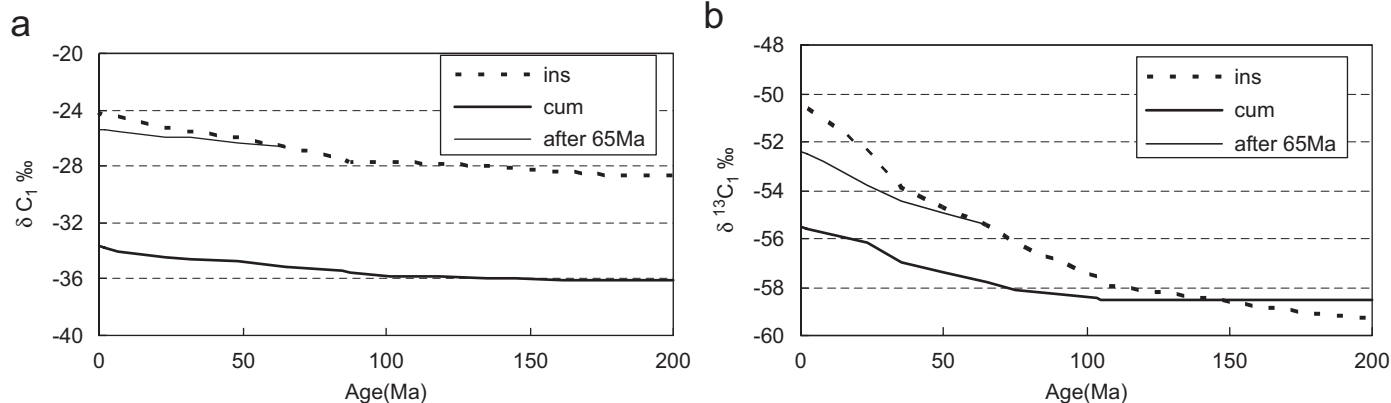

Fig. 8. Plots showing the carbon isotopic composition of methane accumulated since 65 Ma for kerogen-cracking gas from lower Ordovician bottom (a) and oil-cracking gas from paleo-oil pools in mid-upper Ordovician reservoirs, 1000 m from the top of lower Ordovician strata (b). This method is after the Rooney model (Rooney et al., 1995; Cramer et al., 2001).
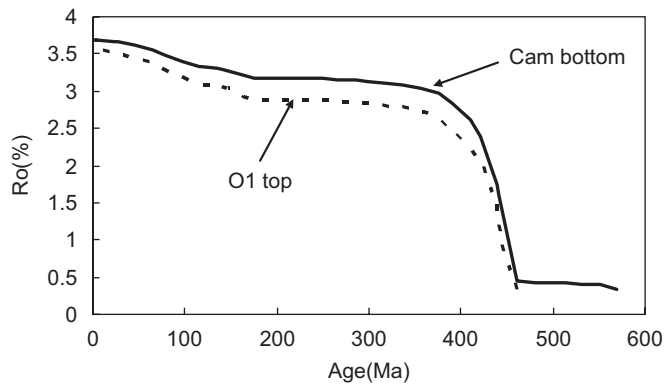
Fig. 9. Thermal maturity curve for the Cambrian–lower Ordovician source rocks in the Yingjisu Depression center. The equivalent vitrinite reflectance was calculated using the modified Easy%Ro method of Tang et al. (1996).

paleo-pools (1000 m from the top of the lower Ordovician strata, see Section 5.2) was only 0.675 at 65 Ma. This extent of cracking indicates that the independent oil phase begins to disappear and both oil and gas occur together as gas condensate (Waples, 2000). Zhang et al. (2004a) and Zhao et al. (2005) analyzed and quantified the diamondoid hydrocarbons in the gas condensate of the YN2 gas pool and found that the gas condensate originated from a crude oil with a cracking extent of approximately 60–70%. This also supports the hypothesis that the gas condensate was formed from cracked oils in the paleo-oil pools in the mid-upper Ordovician strata, not the Cambrian–lower Ordovician strata.

6.3. Source of nitrogen gas

As mentioned above, the natural gas from the YN2 gas pool has a nitrogen gas content of 13.67–17.87%. As only
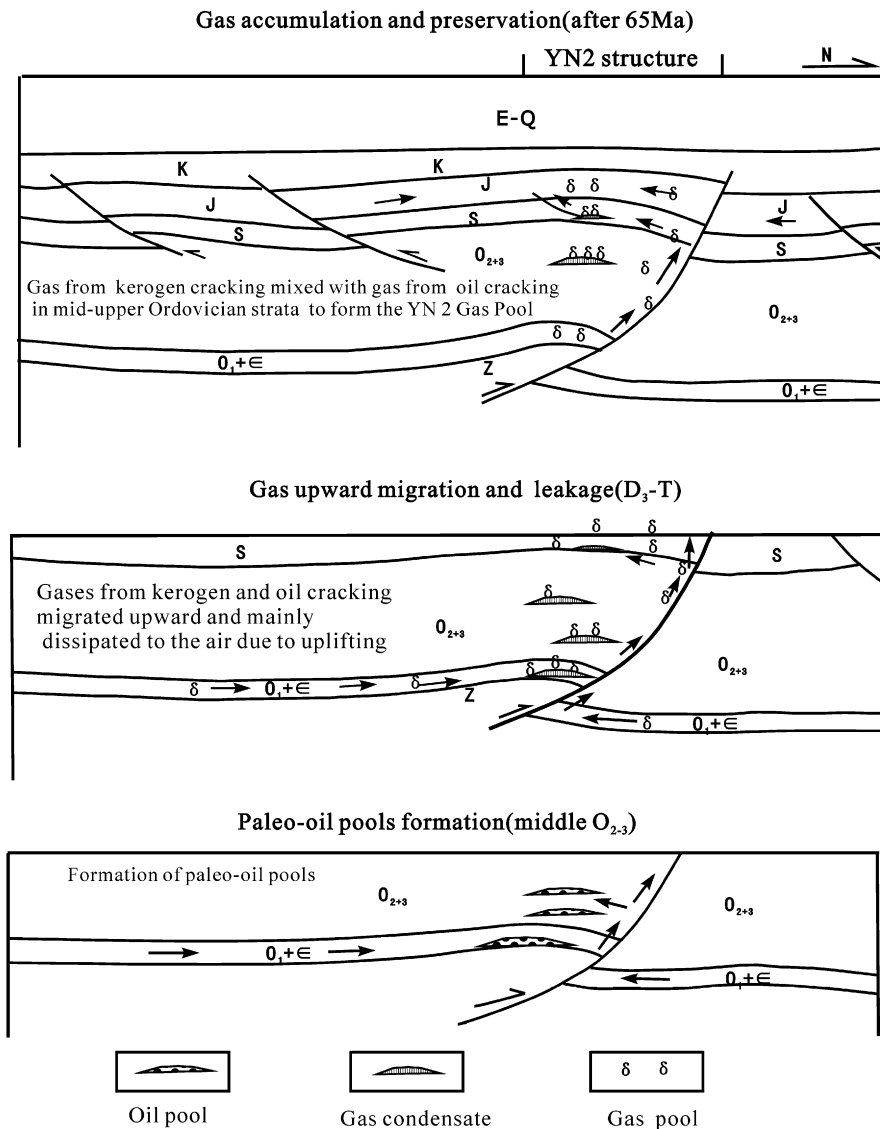

Fig. 10. Schematic model illustrating the formation and evolution of the YN2 gas pool. The structural evolution was modified from Wang and Xu (2005).

minor nitrogen gas is yielded from oil cracking (Li et al., 2003), the nitrogen gas should be mainly derived from the late cracking of kerogen. Littke et al. (1995) found that for coaly and muddy source rocks, the nitrogen gas yields will exceed that of methane when the vitrinite reflectance is over 3.0%. Li et al. (2003) reported similar results based on the pyroysis of muddy source rocks of high maturity from the well TD2. The Cambrian–lower Ordovician source rocks in the Yingjisu Depression are dominated by black and gray mudstones that have been matured to a very high level with a present equivalent vitrinite reflectance up to 3.7% in the depression center (Fig. 9). They would have yielded nitrogen-dominated natural gases during the late stage of gas pool formation. The nitrogen-dominated natural gases must have migrated into the YN2 trap structure and mixed with hydrocarbon-dominated gases from the oil and kerogen cracking to form the high nitrogen content natural gases.

6.4. Accumulation model of the YN2 gas pool

Based on the geological evolution of the YN2 gas pool, and the kinetic modeling results of gas generation and methane carbon isotopic fractionation from the well YN2, an accumulation model and history of the gas pool are suggested (Fig. 10). The main ideas may be summarized as follows:

(1) During the early and middle Ordovician, oils generated from the Cambrian–lower Ordovician source rocks accumulated in the Cambrian–Ordovician strata to form paleo-oil pools.
(2) During the late Ordovician to early Devonian, both the source rock and oils in the Cambrian–lower Ordovician strata were cracked to form gases. Most of these gases were dispersed either by uplifting during the period of Carboniferous to Triassic or by faulting activity in the late Jurassic.
(3) After the Cretaceous, and especially in the Tertiary, the kerogen in Cambrian–lower Ordovician source rocks and oils in mid-upper Ordovician strata re-generated gases. Nitrogen-rich gas from the cracking of kerogen and wet gases from oil-cracking mixed together, and accumulated in the Jurassic trap structure to form the YN2 gas pool.

7. Conclusions

An investigation of the geological and geochemical characteristics of the YN2 gas pool and the establishment of geological models of the gas generation and methane carbon isotopic fractionation of the source rock and the crude oil from the well YN2 lead to the following conclusions:

(1) Natural gas of the YN2 gas pool has a mixed origin from kerogen-generated gas from the Cambrian–lower

Ordovician source rocks and oil-cracking gas from paleo-oil pools in mid-upper Ordovician strata, with estimated proportions of 55% and 45%, respectively.
(2) The gas condensate was mainly derived from oil cracking in the mid-upper Ordovician paleo-pools and the nitrogen gas was mainly derived from the late cracking of the kerogen of the source rocks in the depression center. The wet, isotopically light oil-cracking gas mixed with the dry, nitrogen-rich and isotopically heavy keorgen-generated gas to form the YN2 natural gas with high wetness, nitrogen gas content and a heavier methane carbon isotopic value.
(3) The YN2 area has experienced three stages of evolution: oil and gas generation from the source rocks followed by oil cracking during the early Paleozoic; gas leaking owing to either the long period of uplifting during the late Devonian to Triassic or the faulting activity in the late Jurassic; and formation of the YN2 trap structure, re-generation of gases from the source rocks and the oils in mid-upper Ordovician strata, and formation of the YN2 gas pool during the period of Cretaceous to Quaternary.

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