Chinese Science Bulletin 2004 Vol. 49 Supp. I 66—71

Factors controlling the enrichment of natural gas in Kuche depression, Tarim Basin, NW China: Molecular geochemical evidence from sedimentary organic matter

SUN Yongge[1], XIAO Zhongyao[2], LIU Dehan[1], CHAI Pingxia[1] & XU Shiping[1]

1. SKLOG, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China;
2. Tarim Petroleum Exploration and Development Company, PetroChina, Kuerle 841000, China

Correspondence should be addressed to Sun Yongge (e-mail: ygsun@gig.ac.cn)

Abstract **Using molecular geochemical data from infrared spectrometer and pyrolysis gas chromatography-mass spectrometry, this paper investigates the petroleum generation characteristics of Jurassic coal measures from Kuche depression, Tarim Basin, NW China. The results showed that the Jurassic coaly rocks with medium maturity (R_o%: 0.8—1.1) were enriched in gas-prone functionalities ($-CH_3$) and low molecular weight pyrolysates (<nC_{21}), indicating that the coaly rocks from Kuche depression were gas/condensate prone at the stages of middle to high maturation, and it was further supported by the oil/source correlation from well Yinan 2 in this region.**

Keywords: natural gas, Jurassic coal measures, Kuche depression, infrared spectrometer, pyrolysis gas chromatography-mass spectrometry.

DOI: 10.1360/04wd0339

1 Introduction

The Kuche depression, located in the north part of Tarim Basin, is a foreland depression with a Cenozoic-Mesozoic terrestrial detrital deposit. The general stratigraphic sequence in this depression includes Triassic, Jurassic, Cretaceous, Lower Tertiary, Upper Tertiary and Quaternary strata with a maximum burial depth of over 8000 m (from the bottom to top). Marked with the discovery of a giant gas field, Kela 2, a successive breakthrough in oil and gas exploration has been achieved in this depression in recent years. To date, the proved and workable gas reserves are over 5000×10^8 m^3 accompanied by small quantities of condensate and black oil, and GOR (gas to oil ratio) reaches 1 ∶ 5.6. This depression has become the main source for the project of "Transport Natural Gas from the West to East in China".

Previous studies showed that the Jurassic coal measures and Triassic lacustrine sediments are the main source strata for petroleum discovered to date in the Kuche depression. However, it is difficult to get deeper insight into the petroleum generation characteristics due to the deep burial and high maturity of the purported source rocks. Although the integrated data from geological and geochemical survey have well defined the Middle and Lower Jurassic coal measures as the main source for natural gas discovered to date in Kuche depression, and natural gas was considered to be derived from the middle to high mature stage of coaly rocks[1—4], it is still unclear for mechanisms controlling the gas generation from coaly rocks in Kuche depression. The early-published results suggested that the great thickness of coal-bearing deposit with an appropriate maturation is a main factor accounting for the formation of gas-prone depression[5,6]. The more recent study, however, emphasized maturation as the main driving force for the formation of gas-prone depression[2]. Using infrared spectrometer and pyrolysis gas chromatography-mass spectrometry, this study will investigate at the molecule level why the Lower to Middle Jurassic coaly rocks were gas-prone source rocks during their thermal evolution.

2 Samples and experiments

Due to deep burial and high to over maturity of core samples and severe weathering of the outcrop samples, samples suitable for molecular geochemical analysis is relatively rare. The Lower and Middle Jurassic coaly rocks examined here were collected from the drilled wells in the Iqikelike structural belt, with a maturity range of 0.8—1.1 R_o% (Table 1).

Pyrolysis gas chromatography-mass spectrometry (py-gc-ms) analysis was performed on a CDS 2000-Voyager 1000 GC/MS system. The pyrolysis temperature was programmed from 250℃ (3 min) to 610℃ at 5℃/ms and hold at 610℃ for 10 s. A DB-5 MS capillary column was used with Helium (constant flow rate of 1 mL/min) as the carrier gas and a split ratio of 1/30. The oven temperature was programmed from 30℃ to 300℃ at 3℃/min with an initial holding time of 5 min and a final holding time of 10 min. The mass spectrometer was operated in electron impact mode with the ionizing energy of 70 eV, full scanning from 50 to 600 Dalton. Identification of individual compound was done by comparing the mass spectrum with those of standards or data from publications.

Infared spectrometry analysis was performed on a Perking-Elmer 1725X Fourier Transform Spectrometer and the spectra from 4000 to 300 cm^{-1} region were recorded with a resolution of 4 cm^{-1}. Using maximum likelihood spectral restoration software from Spectrum Square Associate, Inc., the band centers for the C-H_x stretching vibrations on the region of 3000—2800 cm^{-1}

Table 1 Sample background and bulk geochemical data

Sample	Well No.	Depth/m	S_1/mg • g^{-1}	S_2/mg • g^{-1}	T_{max}/℃	IH/mg • g^{-1}	TOC (%)	R_o (%)	–CH (%)	$-CH_2$ (%)	$-CH_3$ (%)
K016	Coal mine	–	1.66	19.58	425	27	71.50	1.02	6.84	48.35	15.44
K041	Yinan 2	4249.98—4250.4	2.00	44.12	445	54	81.30	–	3.91	37.56	28.90
K042	Yinan 2	4315.16—4315.45	0.42	4.06	440	128	3.18	1.05	1.77	39.46	23.36
K043	Yinan 2	4316.60—4317.50	10.71	179.3	437	222	80.70	1.03	9.29	39.41	22.37
K044	Yinan 2	4320.63—4321.26	0.09	0.56	439	57	0.99	–	2.82	37.73	23.47
K045	Yinan 2	4400.26—4408.32	0.43	2.54	445	73	3.47	–	3.32	40.62	22.33
K046	Yinan 2	4400.26—4408.32	0.48	2.22	445	79	2.80	–	3.10	40.96	21.10
K047	Yinan 4	3881—3889.4	0.26	3.16	442	88	3.60	–	3.21	44.71	17.89
K048	Yixi 1	1711	0.06	0.22	487	23	0.95	–	2.15	38.45	31.19
K049	Yixi 1	2903.8	0.18	1.36	441	65	2.10	–	7.46	40.59	20.19
K050	Yixi 1	2906	–	–	–	–	–	–	2.75	37.67	23.84
K051	Yixi 1	2974.6	0.22	1.22	455	46	2.66	–	2.92	37.23	24.38
K052	Yishen 4	3369.8	–	–	–	–	–	–	2.70	39.70	24.78
K014	Yinan 2	5245.36	0.05	0.18	476	26	0.69	–	–	–	–

were deconvoluted and used in band fitting algorithm. Peakfit 4.0 was used to integrate the peak areas.

3 Results and discussion

Screening analysis of core samples from well Yinan 2 suggested that the Jurassic coal measures had high potential of hydrocarbon generation. The results showed that the total organic carbon content (TOC%) of most of the carbonaceous shales of Kezinuer formation was above 20% with a hydrocarbon generated potential of over 35 mg/g. The TOC of coals was in the range of 50%—60% with hydrocarbon generated potential of 100 mg/g to 150 mg/g. Because the present maturity of Jurassic core samples from well Yinan 2 ranged from 0.8 to 1.1 R_o%, it can be evaluated as a suit of good source rock[7—9].

Figure 1 demonstrates the py-gc-ms characteristics (C_8+ total ion chromatograms) of kerogens extracted from the Jurassic coaly rocks. Principally, the py-gc-ms for the studied coals and coaly shales characterized by the following compound classes: alkanes/alkenes, isoprenoids, aromatic hydrocarbons, phenolic and other heteroatomic-containing compounds. It was very clear that all of chromatograms were characterized by a relatively high concentration of aromatic and phenolic compounds, indicating a typical mire environment for source rock development (Fig. 1, left)[10,11]. On the other hand, the concentration of normal alkanes and alkenes is relatively low with a predominance of $< nC_{17}$ homologues (Fig. 1, right). Because the py-gc-ms technique breaks down kerogen in a flash way, it minimizes possible secondary reactions and leaves the products in their "intact" bonding states in the kerogens. This technique has been extensively applied in the assessment of petroleum generation characteristics from sedimentary organic matter. For example, relative concentrations of C_1-nC_5 total hydrocarbons, nC_6-nC_{15} alkanes+alkenes, and nC_{15}^+ alkanes+alkenes in the pyrolysis product have been used to predict oil and gas generation characteristics[12,13]. Although this study did not examine the light hydrocarbons ($<nC_7$) in the pyrolysis products, the predominant distribution of short chain alkanes/alkenes, relatively high concentrations of aromatics and phenolic compounds had already highlighted that the studied source rocks should be gas-prone with small condensates during its further thermal evolution.

It is well known that the relative contents of the methyl ($-CH_3$), methylene ($-CH_2$) and tertiary carbon (–CH) groups bonding to the kerogen network can determine the petroleum generation characteristics of source rock at the molecule level. Theoretically, a relatively high concentration of methyl group is favorable for gas generation, while increasing concentrations of methylene and tertiary carbon groups will shift to the oil generation. Although there is no effective method to determine the absolute concentration of these radicals in macromolecules, using infrared spectrometer, it is possible to deconvolute and curve fit the C-H_x stretching vibration region, then intensities of individual C-H_x bands can be measured[14]. In order to infer the petroleum generation characteristics of source rock, the 2800—3000 cm^{-1} band, representing the stretching vibration of the C-H_x bond in alkyl groups such as –CH, $-CH_2$ and $-CH_3$, was resolved into five bands (Fig. 2): the $-CH_3$ asymmetric and symmetric vibrations occur near 2959 and 2866 cm^{-1}, the $-CH_2$ asymmetric and symmetric vibrations occur near 2919 and 2853 cm^{-1}, the –CH stretching vibration occurs near 2895 cm^{-1} respectively. The 2919 cm^{-1} absorption also contains $-CH_3$ vibration, but to a less extent.

Table 1 lists the ratios of integrated peak areas of ~2958, ~2924 and ~2895 cm^{-1}, representing the relative percentage of the three components, –CH, $-CH_2$ and $-CH_3$ within the band range of 2800—3000 cm^{-1}. The oil and gas-prone trend are clearly shown in Fig. 3. For the convenience of discussion, samples deposited in different depositional setting types from different basins were taken as a reference. The sample set includes the Lower and

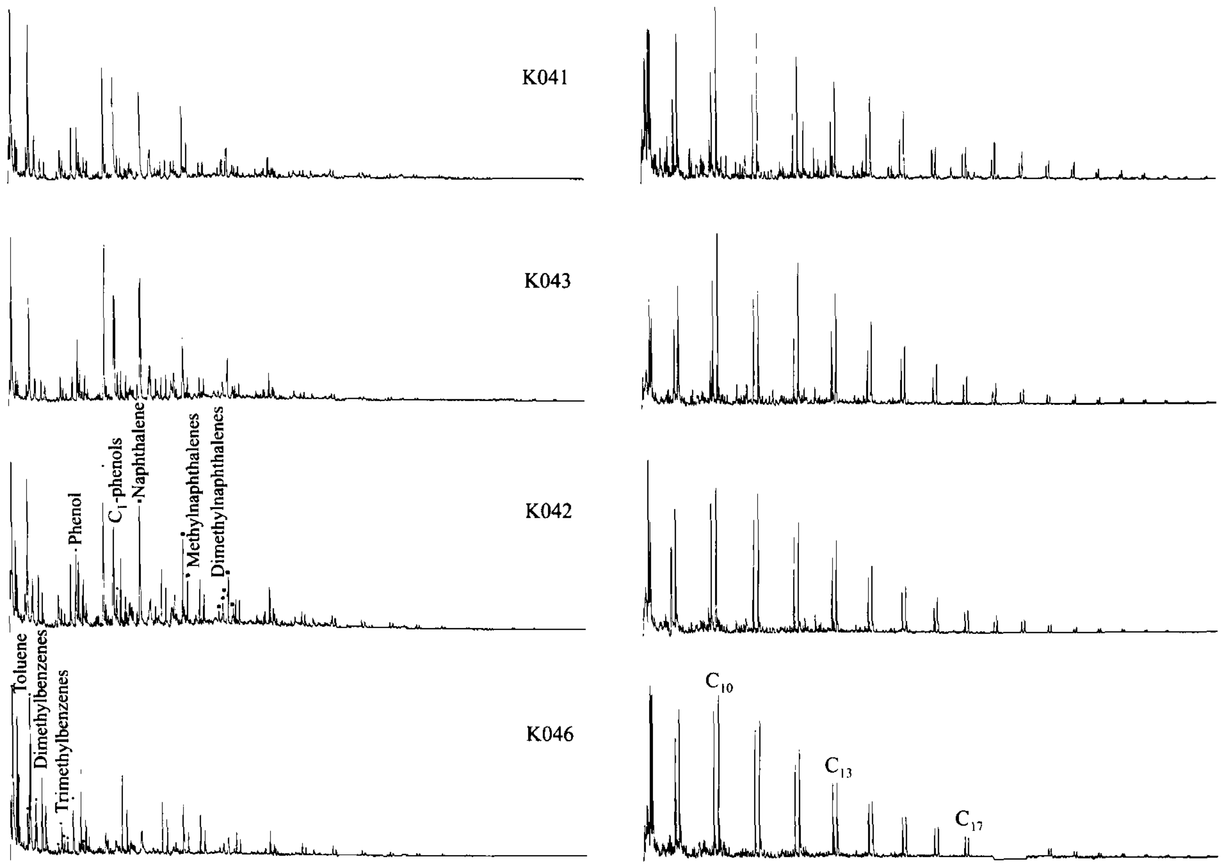

Fig. 1. Representatives of pyrolysis gas chromatograms of kerogens extracted from coals and coaly shales from Kuche depression.

Middle Jurassic coaly rocks from Turpan Basin and Tertiary lacustrine source rocks from Bohai Bay Basin with a maturity range of 0.5—0.9 $R_o\%$, and the latter was just taken as a reference of oil-prone source rock. It can be seen from this diagram that the relative concentration of $-CH_3$ in kerogens increases in the order as deep lacustrine source rocks → Jurassic coaly rocks of Turpan Basin → Iqikelike coaly rocks of Kuche depression, indicating a gas-prone trend. Obviously, the Middle and Lower Jurassic coaly rocks from Turpan Basin is more oil-prone than that of Kuche depression, and this is in consistent with the exploration results, and it was also revealed by relatively high concentrations of alkanes/alkenes in the pyrolysates except aromatic and phenolic compounds in the Middle and Lower Jurassic coaly rocks from Turpan Basin[11,15]. Explorations proved that Turpan Basin is a typical coal-generated oil basin, whereas the Kuche depression is a typical coal-generated gas basin[5,6]. Despite of the varying thermal histories experienced for the Middle and Lower Jurassic coaly rocks in these two basins, which may affect the infrared spectrometric measurements of the relative concentrations of the oil and gas-prone groups, the relative concentrations of the gas-prone radicals have shown, and at least, that the source rocks from Kuche depression with thermal maturity of 0.8—1.1 $R_o\%$ are gas-prone during their further thermal evolution. The present maturity of the Middle and Lower Jurassic coaly rocks from Turpan Basin mainly lay between 0.5—1.3 $R_o\%$[16], whereas those from Kuche depression ranged from 0.7—2.3 $R_o\%$. Due to a significant difference of thermal maturity between source rocks from Turpan Basin and Kuche depression, Liang et al.[2] concluded that the maturation, rather than the organic type, is a main factor to control the enrichment of natural gas in the Kuche depression. However, it is still unambiguous that to what extent the organic type affects the oil and gas generation characteristics of coaly rocks from Kuche depression. The following example of oil/source correlation from well Yinan 2 gave clues for this question.

Drilled test of well Yinan 2 showed that there was a high production of natural gas accompanied by small quantities of condensates. The gas was composed of 82.78%—94.41% of methane and 2.15%—10.02% of heavier hydrocarbons, indicating a wet gas. The stable carbon isotopic analysis of gas components showed that (see Table 2) the isotopic composition of Yinan 2 gas is consistent with that of the Iqikelike gas that originated from Jurassic coal measures. Calculating with the empiri-

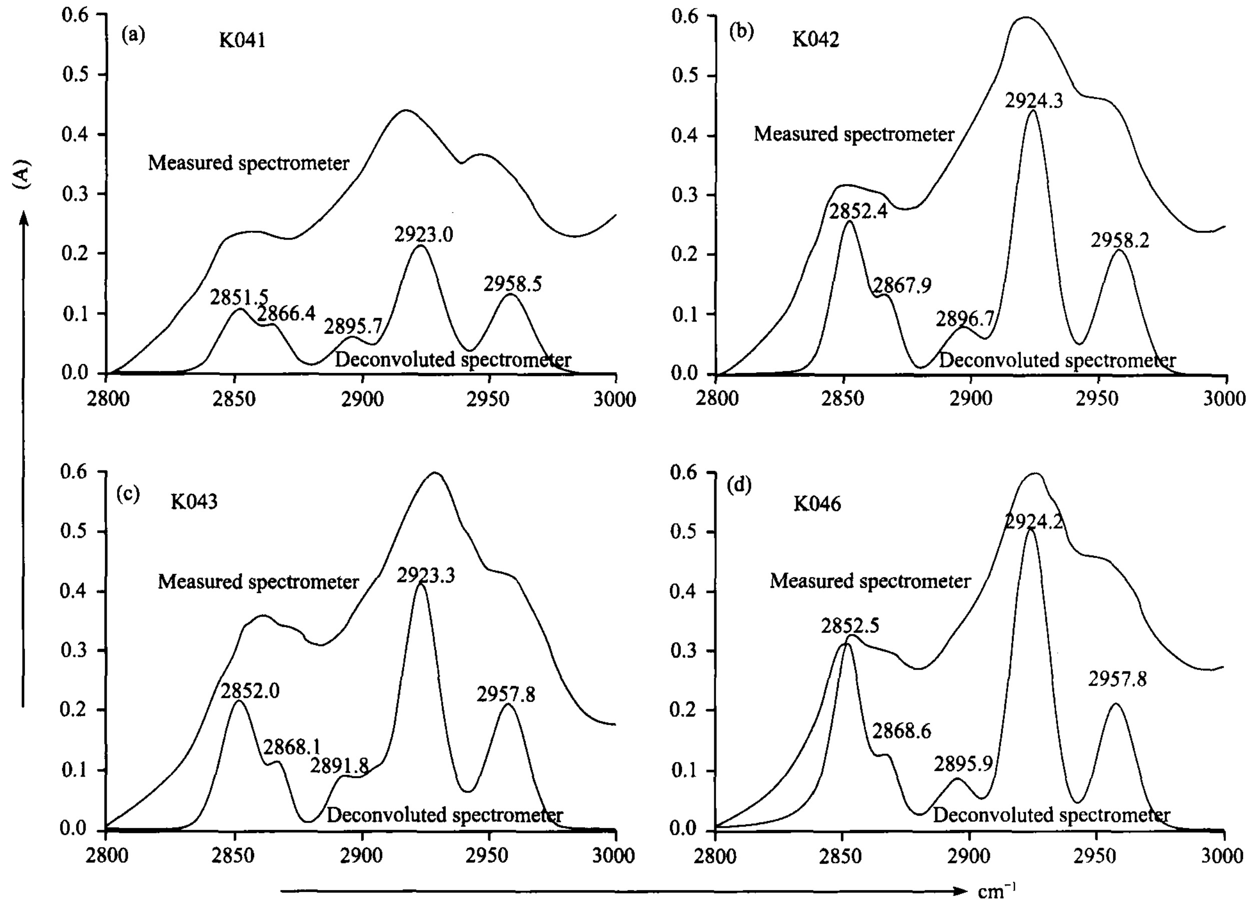

Fig. 2. The C-H_x stretching vibrations on the region of 2800—3000 cm^{-1} of kerogens extracted from coals and coaly shales from Kuche depression.

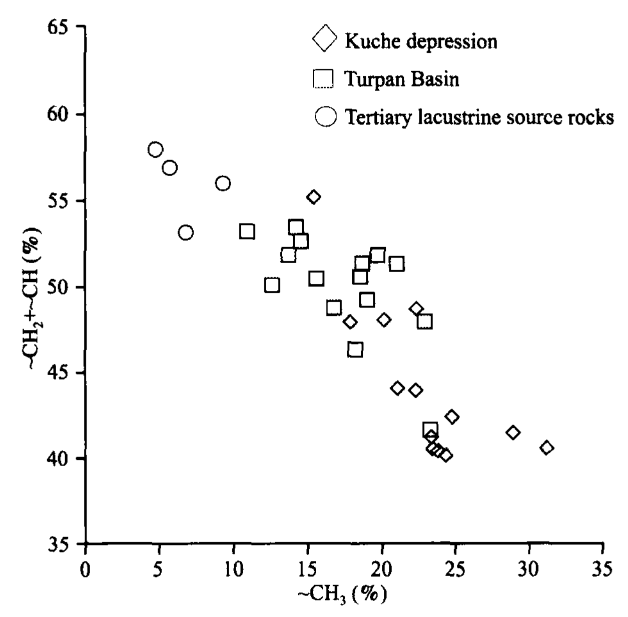

Fig. 3. Relative intensities of individual C-H_x bands in kerogens from coals and coaly shales from Kuche depression.

cal $\delta^{13}C_1$-R_o formula, the Yinan 2 gas has reached a mature stage of 0.94—1.45 R_o%. Therefore, the Yinan 2 gas can be considered as the product of Jurassic coaly rocks at the middle to high thermal maturation. However, the biomarker assemblage of accompanied condensate revealed that this condensate originated from Triassic lacustrine source rocks, which is characterized by low Pristane/Phytane ratio, relatively high concentration of gamacerane, no predominance of the C_{27} and C_{29} sterane distribution. The above-mentioned biomarker assemblage is similar to those of Triassic lacustrine source rocks, but significantly different from those of Jurassic coaly rocks (Fig. 4). Fluid inclusion from reservoir rocks further proved that the oil and gas accumulations of Yinan 2 were derived from two-phase generation with different source strata. Homogeneous temperatures of fluid inclusions can be divided into three groups. The first group ranging from 85℃—116 ℃ (mean ±92℃), corresponding to the oil generation, is majored in coarse green-blue fluorescent organic inclusions which disappear once being heated and have higher gas/liquid ratios. The other two groups are gas or non-fluorescent saline inclusions. The second group with

Table 2 Carbon Isotopic Compositions of Natural gas from Iqikelike Structural Belt

Well No.	Reservoir age	Depth/m	$\delta^{13}C_1$ (‰)	$\delta^{13}C_2$ (‰)	$\delta^{13}C_3$ (‰)	$\delta^{13}C_4$ (‰)
Yinan 2	J_1a	4776—4785	−32.20	−24.55	−23.07	−22.78
Yinan 2C	J_1y	4606—4620	−35.99	−27.56	−24.35	−23.61
Yinan 4	J_1y	3619—3677	−30.67	−25.76	−24.39	−25.44
Yinan 2	J_1a	4578—4783	−34.8	−22.4	−25.9	−21.7
Yi 6	–	–	−33.4	−24.6	−22.3	–
Yi 464	–	–	−34.8	−25.7	−24.4	–

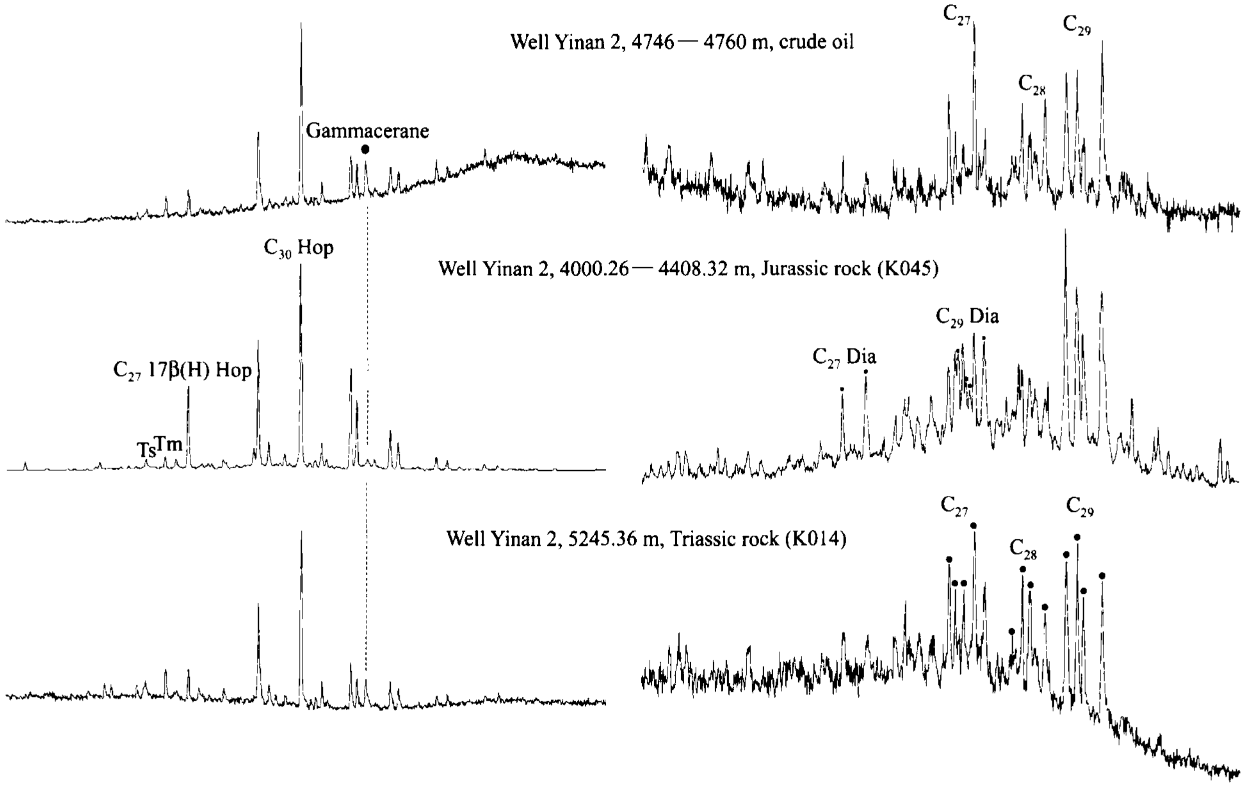

Fig. 4. Oil/source correlation of Well Yinan 2, Kuche depression.

lower gas/liquid ratios was probably formed in the phase of gas accumulation because their maturity was equal to that of the natural gas. Commonly they were 3—5 μm in size and the homogeneous temperatures ranged from 120℃ to 145℃ (mean ±133℃). The third group mainly consists of tiny non-fluorescent saline inclusions with higher homogeneous temperatures of 150—175℃ (mean ±160℃). They may exist as the remains of certain abnormal heat flow events. As for the contribution of Jurassic source rocks to the accumulation of liquid hydrocarbons, it can only be verified from microscope fluorescence observation of reservoir rocks. Corresponding to the green-blue fluorescent organic liquid inclusions mentioned above, there are green-blue fluorescent bitumen and a few of yellow fluorescent bitumen in the sandstones. This may imply that the Jurassic source rocks possibly had a minor contribution to the liquid hydrocarbon accumulation within Yinan 2 reservoir.

Previous studies related to the hydrocarbon generation history of the Middle and Lower Jurassic coaly rocks and trap development history in Iqikelike tectonic belt showed that the Jurassic strata of Kezilenuer formation and Yangxia formation reached peak generation during 6—10 Ma. The seismic data of DQ97-268 line revealed that the growth fault (Kangcun formation and Kuche formation) in the south of Iqikelike anticline was formed in 16.9—5 Ma[1)], and it matches very well with the hydrocarbon generation history. However, oil/source correlation of Yinan 2 showed that there is no commercial accumulation of liquid hydrocarbon from the Middle and Lower Jurassic coaly

1) Lu Fuhua et al., unpublished data.

rocks, indicating that the main product generated from Jurassic coaly rocks is natural gas. Despite of the influences of thermal alteration, it can be seen from the above discussion that for the Middle and Lower Jurassic coaly rocks with maturity in the range of 0.8—1.1 R_o%, the relative concentration of gas-prone groups truely reflects the oil and gas generation characteristics from sedimentary organic matter. Overlapping of samples from Turpan Basin and Kuche depression in Fig. 3 does not mean that the Middle and Lower Jurassic coaly rocks of Kuche depression had a high potential of oil generation, in contrast, it suggested that there were some transitional characteristics of Jurassic coaly rocks between Turpan Basin and Kuche depression.

4 Conclusions

Infrared spectrometer and py-gc-ms analysis show that the pyrolysates of medium mature Jurassic coaly rocks (R_o%: 0.8—1.1) from Kuche depression, Tarim Basin contain significant quantities of gas-prone functionality ($-CH_3$) and short chain alkanes/alkenes ($<nC_{21}$), indicating that the Jurassic coaly rocks are gas-prone with a small potion of condensates during their further thermal evolution. With an example of oil/source correlation from well Yinan 2, it is further confirmed that the Middle and Lower Jurassic coaly rocks are gas-prone.

Despite of the influence of thermal alteration on the relative concentrations of gas-prone radicals, the gas-prone radical's content of type III organic matter is well preserved before peak generation (R_o% = 0.9—1.1), and it can be used to infer the petroleum generation characteristics from sedimentary organic matter.

Acknowledgements The authors greatly thank Prof. Liang Digang of China National Petroleum Corporation for his guiding through this work. This work was co-supported by the Knowledge Innovation Program of the Chinese Academy of Sciences (Grant No. KZCX2-110-2) and the State Scientific and Technological Key Program of the Ninth Five-Year Plan, Oil and Gas exploration in Tarim Basin (Grant No. 99-111-01-03-02).

References

1. Jia, C. Z., Gu, J. Y., Zhang, G. Y., Geological constraints of giant and medium-sized gas fields in Kuqa depression, Chinese Science Bulletin, 2002, 47(suppl.): 47—54.
2. Liang, D. G., Zhang, S. C., Zhao, M. J. et al., Hydrocarbon sources and stages of reservoir formation in Kuqa depression, Tarim Basin, Chinese Science Bulletin, 2002, 47(suppl.): 62—70.
3. Song, Y., Jia, C. Z., Zhao, M. J. et al., Controlling factors for large gas field formation in thrust belt of Kuqa coal derived hydrocarbon foreland basin, Chinese Science Bulletin, 2002, 47(suppl.): 55—61.
4. Sun, Y., Liu, D., Fan, S. et al., Gas generated and accumulated in a large, ultra-high pressured gas reservoir of china: integration of geochemical and geological data, in Abstract of 20th International Meeting on Organic Geochemistry, UMR 7566 GZR, Universite Henri Poincare, France, 2001, 146—147.
5. Dai, J., He, B., Sun, Y. et al., Formation of the central-Asia coal-formed gas accumulation domain and its source rocks, Petroleum Exploration and Development (in Chinese), 1995, 22(3): 1—6.
6. Dai, J., Li, X., Characteristics of coal-formed gas accumulation belts in the east part of the central-Asia coal-formed gas accumulation domain, Exploration and Development (in Chinese), 1995, 22(5): 1—7.
7. Chen, J., Zhao, W., Qin, Y. et al., Petroleum formation in Jurassic coal-bearing basins, Northwest China (Part 1), Exploration and Development (in Chinese), 1998, 25(3): 1—5.
8. Chen, J., Zhao, W., Qin, Y. et al., Petroleum formation in Jurassic coal-bearing basins, Northwest China (Part 2), Exploration and Development (in Chinese), 1998, 25(4): 3—6.
9. Chen, J., Zhao, W., Qin, Y. et al., Petroleum formation in Jurassic coal-bearing basins, Northwest China (Part 3), Exploration and Development (in Chinese), 1998, 25(5): 3—7.
10. Larter, S., Application of analytical pyrolysis techniques to kerogen characterization and fossil fuel exploration/exploitation, in Analytical Pyrolysis: Techniques and Applications (ed. Voorhees, K. J.), Southampton: Butterworth & Co LTD, 1984, 212—276.
11. Sun, Y., Zhu, J., Xu, H. et al., Environmental constraints on oil-generating coals, Geochemistry (in Chinese), 2002, 31(1): 8—14.
12. Sun, Y., Sheng, G., Fu, J., Application of pyrolysis gas chromatography technique to evaluation of coal-generated hydrocarbon, Science in China, Ser. D, 1997, 40(1): 99—103.
13. Horsfield, B., Practical criteria for classifying kerogens: some observations from pyrolysis-gas chromatography, Geochimica et Cosmochimica Acta, 1989, 53(4): 891—901.
14. Lin, R., Patric, R., Studying individual macerals using I. R. microspectroscopy, and implications on oil versus gas/condensate proneness and low-rank generation, Organic Geochemistry, 1993, 20(6): 695—706.
15. Sun, Y., Sheng, G., Peng, P. et al., Compound-specific analysis as a tool for correlating coal-sourced oils and interbedded shale-sourced oils in coal measures: an example form Turpan Basin, Organic Geochemistry, 2000, 31(12): 1349—1362.
16. Liang, D., Zhang, S., Chen, J. et al., Organic geochemistry of oil and gas in the Kuqa depression, Tarim Basin, NW China, Organic Geochemistry, 2003, 34(7): 873—888.

(Received August 5, 2004; accepted November 11, 2004)