CHINESE JOURNAL OF GEOCHEMISTRY Vol. 26 No. 1 2007

DOI: 10.1007/s11631-007-0066-y

Experiments on the primary migration of oil from source rocks

MA Suping (马素萍)[1,2], LEI Tianzhu (雷天柱)[1,2], JIN Ming (荆明)[1,2], and XIA Yanqing (夏燕青)[1*]

[1] *Key Laboratory o f Gas Geochemistry，Institute of Geology and Geophysics，Chinese Academy of Sciences, Lanzhou 730000, China*

[2] *Graduate School，Chinese Academy of Sciences，Beijing 100039，China*

* *Corresponding author, E-mail: yqxia@lzb.ac.cn*

Received October 13, 2005; accepted December 8, 2005

Abstract Simulation experiments on the primary migration of oil were carried out on massive samples. The results proved that oil generated from source rocks was expelled in the form of an independent oil phase. High oil-expulsion efficiency was observed. It follows that the primary migration of oil is not directly dependent on the quantity of oil generated from the source rocks. Therefore, the oil-expulsion proportion was high though some source rocks yielded only a limited amount of oil. A great deal of gas was produced at the same time of oil-generation. Thus, it can be concluded that the main expulsion energy for oil primary migration came from these gases.

Key words source rock; primary migration; expulsion efficiency; simulation experiment

1 Introduction

Oil and gas are the combustible mineral resources, and the locus of their generation is remote from the reservoir. The formation of oil and gas fields refers to the whole process of hydrocarbon generation, migration and accumulation. The primary migration of hydrocarbons is a bridge between oil generation and accumulation and thus, is of great importance. Only when hydrocarbons are generated from source rocks and are accumulated to a certain extent, will the hydrocarbon reservoir be formed. Illing (1933) presented the concept of petroleum migration. After that, many scholars devoted themselves to the study of hydrocarbon migration (Tissot and Welte, 1978; Chen Heli et al., 1987; Huang Difan et al., 1988; Wilhelms et al., 1990; Sandvik and Mercer, 1990; Rudkiewicz et al., 1994; Li Mingcheng, 1994; Wang Benshan et al., 1994; Chen et al., 1994). With the development of numerous simulation methods, thermal simulation experiments and detection and analysis techniques such as gas chro- matography, chromatography-mass spectrometry, isotope mass spectrometry, NMR spec- troscopy, pyrogenation, infrared spectroscopy, the understanding of hydrocarbon migration is further improved. Moreover, the application of fluorescence microscopy and the development of fluid inclusions and geochemical correlations between source rocks and oils provide a method for the study of oil migration. However, up to date, the study in this aspect is still a weak link, and many results are qualitative or deductive. Therefore, the questions cannot be solved that which metapelite and carbonate rocks can be regarded as source rocks, and which can form oil/gas reservoirs of industrial importance. The standard of effective source rocks is established as TOC>0.5%. The reason is that only when the TOC contents must exceed 0.5%, can enough hydrocarbons be generated for primary migration to take place. Whether are hydrocarbons expelled from source rocks only after TOC reaches 0.5%? Directing toward this question, we carried out simulation experiments to determine the oil expulsion efficiency.

2 Simulation experiments on hydrocarbon migration

2.1 Fundamental geological circumstances and geochemical characteristics of the samples used for simulation experiments

The samples used in these experiments were low-mature Tertiary source rocks collected from both the Qaidam Basin and Fushun coalfield of China. The basic geological circumstances and geochemical characteristics of the samples are described in Table 1. These rocks are not rich in organic carbon except for

Table 1. Geological characteristics of the samples

Sample No.	Lithology	Horizon	Well No.	Well depth (m)	TOC (%)	R_o (%)	Kerogen type
Q-1	Calcareous mudstone	N	Yueshen-1	2360.0	0.18	0.38	III**
Q-2	Calcareous mudstone	N	Nan-7	1437.32	0.56	0.32	III**
Q-3	Calcareous mudstone	N	Liang-3	1765.1	0.31	0.33	III**
Q-4	Calcareous mudstone	N	Xian-8	2761.09	0.38	0.41	III**
F*	Mudstone	E	/	/	9.70	0.30	I

* Section sample, without well number and well depth; ** they are of type-III, but are better.

the samples collected from the Fushun coalfield.

2.2 Procedure of simulation experiments

At present, thermo-pressure simulation experiments are the main method of simulation used for hydrocarbon migration. That is, by utilizing a device, the geotemperature and geopressure as well as the generation of oil and gas from rocks can be simulated. The simulation experiments on hydrocarbon migration should provide not only the hydrocarbon-generating conditions, but also the hydrocarbon migration conditions. Many scholars have made valuable contributions to the study of the simulation experiments on oil primary migration (Bonilla and Engel, 1988; Krooss and Leythaeuser, 1988; Ao Shanxiang, 1989; Sandvik and Mercer, 1990; Nobuyori Takeda et al., 1990; Lafargue et al., 1990, 1994; Rudkiewicz et al., 1994; Mishra et al., 1997; Shi Ji'an et al., 2005). The simulation experiment on oil primary migration involves two methods. One is based on the observation of oil-expulsion during the process of consolidation and geochemical analysis, to determine the variety of the group components. The other deals with the hydrocarbon generation when the pressure increases in the semi-open and closed systems. Based on the work of the predecessors, the simulation experiments were modified correspondingly in this research.

2.2.1 Method

In his study of the role of mineral matrix in the hydrocarbon-generation, Lewan (1993) heated granular source rocks with water at 300–350℃ and discovered that the distribution pattern of hydrocarbons was very similar to that of crude oils. Since then, he has investigated the effect of water on hydrocarbon generation. Then, the hydrous simulation experiment was considered as an almost actual simulation method for hydrocarbon generation. Using this method, Lewan (1993) simulated the process of hydrocarbon generation but little room was given to hydrocarbon migration. Lafargue et al. (1994) simulated primary migration using compaction and hydrocarbon expulsion experiments. But the conditions under which this simulation method was used were different from the actual ones because no excess water was added in the system.

In this paper, by analyzing a variety of organic geochemistry simulation experiments including hydrocarbon-generation and migration experiments, and learning from the predecessor's strong points to offset their weakness and considering the physical & chemical characteristics of oil and gas migration, the hydrous pyrolysis simulation method was employed to study the massive samples of hydrocarbon source rocks in a closed system. This experimental method can simulate the nature of oil and gas migration under the conditions more approximate to the real ones (Fig. 1). The experiments were carried out at 300℃ and 350℃. The reason is that the amount of hydrocarbons generated was very small at <300℃ and the water turned into one under the supercritical condition when the temperature reached 350℃. In these experiments, the pressure came from the saturated vapor tension.

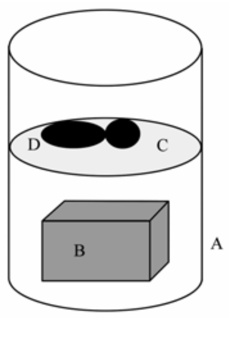

Fig. 1. The sketch showing the simulation experiments on oil primary migration. A. High-pressure autoclave; B. sample (whole); C. water surface; D. oil.

2.2.2 Steps of the thermo-pressure simulation experiments

Used in the experiments was a FYX1 Model high-pressure autoclave manufactured by the Dalian Tongchan Autoclave Vessel Manufacturing Co., Ltd.

Firstly, the wall and lid of the high-pressure autoclave as well as the temperature measuring tube were washed repeatedly with chloroform, tap water and de-ionized water. Then, the samples were put into the autoclave and covered in distilled water. After the samples were loaded, the air in the autoclave was replaced three times by N_2 and the autoclave was evacuated and sealed. After the temperature was raised to its endpoint, it was kept constant for 72 hours. The experimental temperature was controlled by a digital temperature controller, with an error of ±2℃. After the time was over and the high-pressure autoclave was cooled naturally to room temperature, the gaseous pyrogenation products were collected quantitatively by displacement with saturated brine.

2.2.3 Collection of liquid products

When hydrocarbon source rocks were heated, a part of the oil generated was expelled. The other part was named as residual oil, which remained in the rocks. The expelled oil was collected by way of dissolving (floating on the surface of water), extracting (dissolved in the water) and washing (stuck on the wall and lid of the autoclave). The residual oil was recovered by way of chloroform Soxhlet extraction for 72 hours after the heated samples were pulverized to <100 mesh.

2.2.4 Analysis of the products

(i) Gaseous product analysis. Gaseous products were analyzed on an HP-5890 gas chromatograph. The chromatograph conditions are: MS molecular sieve: column (Ø3 mm×2.4 m), GDX-502 column (Ø3 mm×4 m); initial temperature: 30℃; rate: 70℃/min; final temperature: 160℃; carrier gas: Ar 99.999%; inlet pressure: 200 kPa; injector temperature: 120℃; detector: 180℃, detector: TCDFID; injector quantity: 1 mL.

(ii) Liquid product separation. The expelled oil and residual oil were each separated by column chromatography into four fractions: asphaltene, saturated hydrocarbon, aromatic hydrocarbon, non-hydrocarbon. The procedure of oil separation is described as follows: firstly, asphaltene was separated by precipitation with petroleum ether. Then, the residual petroleum ether solute was separated on a column packed with silica gel/alumina (4:1). Saturated hydrocarbons were washed out with petroleum ether. Aromatic hydrocarbons were washed out with dichloromethane, and non-hydrocarbons were washed out with methanol.

3 Results and discussion

3.1 Phase state of oil primary migration

The recovery of gas and free-floating oil indicates that the primary migration has occurred. Moreover, the source rocks maintain their physical integrity (Fig. 2). The system provides an attempt to match the natural expulsion system with oil and gas migrating through pores and microfractures. What are the ways in which oil is expelled from source rocks? Twenty-five years or more ago, some researchers considered that hydrocarbon primary migration occurred as a water solution (Barker, 1977; Price, 1976; McAuliffe, 1978, 1979). Later, others thought that oil was expelled as a separate phase (Dickey, 1975; Magara, 1978). Based on the group composition data of the expelled oil and residual oil (Table 2), it is considered that oil might be expelled in the form of an independent oil phase. Saturated and aromatic hydrocarbons comprise the total hydrocarbon contents (THC). Asphaltene and non-hydrocarbons comprise the polar organic matter. If oil is expelled in water solutions, different solubilities of different components would lead to their separation, and the expelled oil would be enriched in more soluble components and the residual oil would contain more insoluble components. In fact, there is no significant difference between expelled oil and residual oil. By and large, the saturated hydrocarbon contents of the expelled oil are slightly higher and the aromatic hydrocarbon contents of the residual oil are also slightly higher (Fig. 3). Comparing the expelled oil with the residual oil, we found that THC and asphaltene and non-hydrocarbons in these two fractions of oil do not show any significant regular difference. All the evidence indicates that an obvious separation did not occur at the time of oil was expelled in the form of an independent oil phase.

Fig. 2. The regime of F (Fushun oil shale) after primary migration simulation experiment.

Table 2. Relationship between the fraction component contents of expelled oil and those of residual oil

Serial No.*	Category	The group composition of expelled oil and residual oil (%)						Total hydrocarbon/ (non-hydrocarbon+ asphaltene)
		Saturated hydrocarbon	Arene	Non-hydroca -rbon	Asphaltene	Total hydro- carbon	Non-hydro- carbon+ asphaltene	
Q1-300	Expelled oil	30.61	2.55	58.17	8.67	33.16	66.84	0.50
	Residual oil	33.29	7.70	58.8	0.21	40.99	59.01	0.69
Q1-350	Expelled oil	33.97	2.87	52.64	10.52	36.84	63.16	0.58
	Residual oil	12.85	12.85	57.16	17.14	25.7	74.3	0.35
Q2-300	Expelled oil	27.14	5.49	35.42	31.95	32.63	67.37	0.48
	Residual oil	36.65	16.70	44.72	1.93	53.35	46.65	1.14
Q2-350	Expelled oil	43.04	11.36	16.06	29.54	54.4	45.6	1.19
	Residual oil	19.46	11.69	60.8	11.69	31.15	72.49	0.43
Q3-300	Expelled oil	61.38	4.16	26.44	8.05	65.54	34.49	1.90
	Residual oil	35.96	11.61	48.21	4.22	47.57	52.43	0.91
Q3-350	Expelled oil	33.18	8.07	36.78	21.97	41.25	58.75	0.70
	Residual oil	16.94	16.94	50.87	15.25	33.88	66.12	0.51
Q4-300	Expelled oil	34.4	6.45	48.4	10.75	40.85	59.15	0.69
	Residual oil	39.16	8.64	50.87	1.33	47.8	52.2	0.92
Q4-350	Expelled oil	21.13	14.09	41.21	23.57	35.22	64.78	0.54
	Residual oil	72.71	19.32	4.59	3.38	92.03	7.97	11.55
F-300	Expelled oil	36.23	3.41	20.06	40.29	39.64	60.35	0.66
	Residual oil	39.05	13.01	39.23	8.71	52.06	47.94	1.09
F-350	Expelled oil	51.33	9.02	23.21	16.44	60.35	39.65	1.52
	Residual oil	31.36	9.92	45.04	13.68	41.28	58.72	0.70

* Q1, Q2, Q3, Q4 and F are the samples used in the experiments, and 300 and 350 mean the experimental temperatures are 300℃ and 350℃, respectively.

3.2 Efficiency of oil primary migration

The quantity of expelled oil plus the residual oil along with sample weight and TOC (%) provide an oil generation rate per unit of rock and per unit of TOC (Table 3). Based on the oil generation rates of expelled oil and residual oil and the total oil generation rate, the oil expulsion ratio is worked out.

The oil generation rates of the four samples, Q1–Q4, are relatively low (Tables 2 and 3). The maximal oil generation yields for every 100 g of organic carbon does not exceed 10 g. That is because of the poor quality of the source material. The oil generation rate of sample F is only 5.5746 g/100 g organic carbon at 300℃. However, it is 42.1006 g/100 g at 350℃ (Table 3). Although the oil generation rates of most of the samples are not high, the expulsion rates are very high (Table 3). For example, although the expulsion rate of Q4 is the lowest among the samples at 300℃, it still reaches 18.96%. The expulsion rates of most of the samples exceed 50%, and the expulsion rate of sample F even reaches 97.54% at 350℃ (Table 3). Currently, the most commonly accepted viewpoint about hydrocarbon expulsion is that the generated oil must saturate the source rocks. Based on the viewpoint mentioned above, the already generated oil is not expelled from rocks if the TOC of hydrocarbon-generating rocks is less than 0.5%, and the rock is not a potential source rock. But our experiments demonstrated that oil primary migration can occur even when the yield of oil generation is very low. In other words, oil will be expelled from hydrocarbon- generation rocks and will contribute a lot to the formation of oil reservoirs even if their TOC is low.

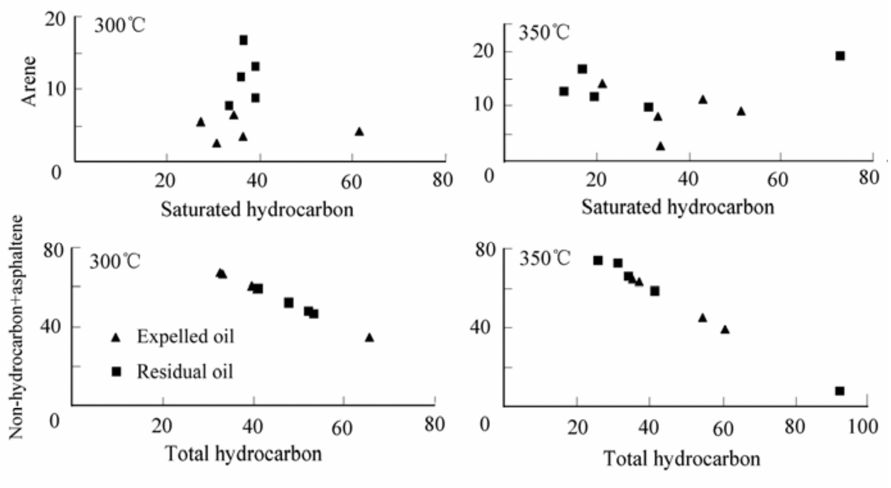

Fig. 3. The relationship between the group components of expelled oil and residual oil.

Table 3. The rates of discharge for expelled oil and residual oil

Serial No.	Production rate for expelled oil and residual oil (g/100 g total rock)		Production rate of oil*		Rate of discharge (%)
			(g/100g whole rock)	(g/100g OC)**	
Q1-300	Expelled oil	0.0079	0.0116	6.4509	68.10
	Residual oil	0.0037			
Q1-350	Expelled oil	0.0087	0.0116	6.4182	75.00
	Residual oil	0.0029			
Q2-300	Expelled oil	0.0115	0.0215	3.8444	53.49
	Residual oil	0.0100			
Q2-350	Expelled oil	0.0299	0.0452	8.0729	66.15
	Residual oil	0.0153			
Q3-300	Expelled oil	0.0143	0.0220	7.1098	64.71
	Residual oil	0.0078			
Q3-350	Expelled oil	0.0089	0.0113	3.6460	78.76
	Residual oil	0.0024			
Q4-300	Expelled oil	0.0040	0.0211	5.5538	18.96
	Residual oil	0.0171			
Q4-350	Expelled oil	0.0138	0.0358	9.4273	38.55
	Residual oil	0.0220			
F-300	Expelled oil	0.2243	0.5407	5.5746	41.48
	Residual oil	0.3164			
F-350	Expelled oil	3.9832	4.0838	42.1006	97.54
	Residual oil	0.1005			

* Expelled oil plus residual oil; ** OC stands for organic carbon.

3.3 Force of oil primary migration

In the process of oil generation, a great deal of gas is generated including CO_2, H_2 and hydrocarbon gases, and the gas-generation rate is above 500 mL/100 g for all rocks (Table 4). The volume of gas generated is much greater than that in the pore space of the rock, so the gases are bound to be expelled, and become the force of oil primary migration.

4 Conclusions

Based on simulation experiments on oil primary migration, some new findings have been made as follows:

(1) Although there are some differences in chemical composition between expelled oil and residual oil, they are not so significant. Thus oil generated from source rocks is expelled in the form of an independent oil phase.

(2) At the time of oil generation, a large amount of gas is generated. These gases may be the main force for oil primary migration.

(3) Even the amount of oil generated is low, oil primary migration still occurs and its efficiency is very high. So the hydrocarbon-generating rocks can expel oil and contribute a lot to the formation of oil reservoirs although their TOC contents are low.

Table 4. The gas yields and gas component contents

Serial No.	Gas yield (mL/100 g whole rock)	Gas component content * (v/v, %)							
		H_2	Ar	O_2	N_2	CO	CO_2	C_1	C_2
Q1-300	507.66	11.27	0.24	7.28	25.98	0.27	54.40	0.40	0.02
Q1-350	631.47	4.10	0.02	0.78	1.71	0.02	92.90	0.28	0.02
Q2-300	666.14	15.99	0.25	7.62	23.64	0.23	51.49	0.51	0.06
Q2-350	760.40	33.16	0.03	0.48	1.20	0.33	60.64	2.33	0.74
Q3-300	1435.42	1.37	0.20	4.40	19.07	/	74.86	0.02	0.004
Q3-350	3355.51	1.23	0.01	0.58	1.17	0.02	96.70	0.19	0.004
Q4-300	546.20	10.55	0.09	1.34	3.71	0.12	83.58	0.46	0.04
Q4-350	688.83	3.56	0.02	0.51	1.07	0.02	93.47	0.92	0.02
F-300	1503.09	11.12	0.06	1.05	3.11	0.05	69.60	5.82	3.24
F-350	1678.56	6.04	0.07	1.00	3.34	0.08	73.02	6.51	3.70

* The contents of heavy hydrocarbons are very low, so not presented here.

Acknowledgements This research project was supported by the Knowledge Innovation Program of the Chinese Academy of Sciences (Grant No. KZCX3-SW-128).

References

Ao Shanxiang (1989) The simulated experiments of source rock maturation and primary migration of crude oil [J]. *Journal of Geology and Geochemistry.* **3**, IX–X (in Chinese with English abstract).

Barker C. (1977) Aqueous solubility of petroleum as applied to its origin and primary migration: Discussion [J]. *Amer. Assoc. Petrol. Geol. Bull*. **61**, 2146–2149.

Bonilla J.V. and Engel M.H. (1988) Chemical alteration of crude oils during simulated migration through quartz and clay minerals [J]. *Organic Geochemistry*. **13**, 503–512.

Chen Heli and Tang Xiyuan (1987) *Petroleum Geology Translation Florilegium, Oil and Gas Migration* (the second series) [M]. Petroleum Industry Press, Beijing (in Chinese).

Chen J.H., Philp R.P., Fu J.M., and Sheng G.Y. (1994) A geochemical study of primary oil migration in Biyang Basin, China [J]. *Journal of Southeast Asian Earth Sciences*. **9**, 207–220.

Dickey P.A. (1975) Possible primary migration of oil from source rock in oil phase [J]. *AAPG Bull*. **59**, 336–345.

Huang Difan, Zhou Guoqing, Li Jinchao, Lu Shu'e et al. (1988) *Petroleum Geology Translation Florilegium, Oil and Gas Migration* (the first series edition) [M]. Petroleum Industry Press, Beijing (in Chinese).

Illing V.C. (1933) Migration of oil and natural gas [J]. *Inst. Petroleum Technology Jour*. **19**, 229–274.

Ismail Ozkaya and Ali Akbar (1991) An interative procedure to determine depth and time of primary oil migration and expulsion efficiency of source rocks [J]. *Journal of Petroleum Science and Engineering*. **5**, 371–378.

Krooss B.M. and Leythaeuser D. (1988) Light hydrocarbon diffusion in a caprock [J]. *Chemical Geology*. **71**, 65–76.

Lafargue W., Espitalie J., Jacobsen T. et al. (1990) Experimental simulation of hydrocarbon expulsion [J]. *Organic Geochemistry*. **16**, 121–131.

Lafargue W., Espitalie J., Broksb T.M. et al. (1994) Experimental simulation of primary migration [J]. *Organic Geochemistry*. **22**, 575–586.

Lewan M.D. (1993) Laboratory simulation of petroleum formation: Hydrous pyrolysis. In *Organic Geochemistry* (eds. M. Engel and S. Macko) [M]. pp.419–442. Plenum Publications Corp., New York.

Li Mingcheng (1994) *Oil and Gas Migration* [M]. Petroleum Industry Press, Beijing (in Chinese).

Magara K. (1978) Significance of the expulsion of water in oil-phase primary migration [J]. *Can. Petrol. Geol. Bull*. **26**, 123–131.

McAuliffe C.D. (1978) Role of solubility in migration of petroleum from source [J]. *AAPG Bull*. **62**, 541–542.

McAuliffe C.D. (1979) Oil and gas migration-chemical and physical constraints [J]. *AAPG Bull*. **63**, 761–781.

Mishra C.S., Samanata U., Gupta A., Thomas N.J., and Misra K.N. (1997) Hydrous pyrolysis of a Type Ⅲ source: Fractionation effects during primary migration in natural and artificially matured samples [J]. *Organic Geochemistry*. **25**, 489–505.

Nobuyori Takeda, Shunji Sato, and Tsutomu Machihara (1990) Study of petroleum generation by compaction pyrolysis—I. Construction of a novel pyrolysis system with compaction and expulsion of pyrolyzate from source rock [J]. *Organic Geochemistry*. **16**, 143–153.

Price L.C. (1976) Aqueous solubility of petroleum as applied to its origin and primary migration [J]. *AAPG Bull*. **60**, 213–224.

Rudkiewicz J.L., Brévart O., Connan J. et al. (1994) Primary migration behavior of hydrocarbons: From laboratory experiments to geological situations through fluid flow models [J]. *Organic Geochemistry*. **22**, 631–639.

Sandvik E.I. and Mercer J.N. (1990) Primary migration by bulk hydrocarbon flow [J]. *Organic Geochemistry*. **16**, 83–89.

Shi Ji'an, Zhao Xin, Wang Qi, and Liu Quanyou (2005) Thermogravimetry-differential thermal analysis coupled with chromatography as a thermal simulation experimental method and its application to gaseous hydrocarbons from different source rocks [J]. *Chinese Journal of Geochemistry*. **24**, 289–296.

Tissot B.P. and Welte D.H. (1978) *Petroleum Formation and Occurrence* [M]. Springer Verlag, Berlin.

Wang Benshan, Cheng Keming, and Ma Wanyi (1994) *Research of Oil and Ga—Analysis of Miyang Basin* [M]. Petroleum Industry Press, Beijing (in Chinese).

Wilhelms A., Larter S.R., Leythaeuser D. et al. (1990) Recognition and quantification of the effects of primary migration in a Jurassic clastic source-rock from the Norwegian continental shelf [J]. *Organic Geochemistry*. **16**, 103–113.