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Geochemical characteristics of noble gases in natural gas and their application in tracing natural gas migration in the middle part of the western Sichuan Depression, China

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Abstract: Noble gases in natural gas, from Xiaoquan, Xinchang, Hexingchang and Fenggu gas reservoirs in the middle part of the western Sichuan Depression, China, were analysed. Results show that the volume content of crustal noble gases accounts for 97.9% to 99.7% of the total noble gas content, indicating that the noble gases in the study area are very largely derived from the crust. Moreover, the ^{40}Ar time-accumulating effect of source rocks is used to determine the complex relationship between gases and source rocks in this area, and the results agree well with that from analysis of source rock light hydrocarbons. Due to the short migration distance, the separation of ^{4}He and ^{40}Ar is not significant in Xujiahe natural gas and Lower and Middle Jurassic natural gas, so it is difficult to trace natural gas migration. However, this separation characteristic of ^{4}He and ^{40}Ar in Middle and Upper Jurassic natural gas is significant, which indicates that natural gas migration was from the Middle Jurassic to Upper Jurassic formations. In addition, the variation trends of $^{3}He/^{4}He$ ratio and $\delta^{13}C_1$ value indicates that natural gas migration is from the Xujiahe formation to the Jurassic layer in the study area.

Key words: Western Sichuan Depression, noble gas, He and Ar isotopes, natural gas migration

1 Introduction

Noble gases belong to the zero group in the periodic table of elements for the reason that they generally do not react with other elements. They are He, Ne, Ar, Kr, Xe and Rn and as well are known as inert gases. According to their different sources, noble gases can be classified into three categories (Ballentine et al, 2002), namely atmosphere-derived nonradiogenic noble gases, such as ^{20}Ne and ^{36}Ar; radiogenic noble gases such as ^{4}He, ^{21}Ne and ^{40}Ar derived from the deep crust, reservoirs or source rock; and mantle-derived noble gases such as ^{3}He. Noble gases from different sources differ significantly in isotopic composition and volume percentage (Torgersen and Kennedy, 1999; Porcelli and Ballentine, 2002; Kennedy et al, 2002). Based on such characteristics, the origins of noble gases can be analysed by qualitative and quantitative methods (Craig et al, 1978; Xu, 1998; Ballentine et al, 2002). For atmosphere-derived noble gases, because their solubilities are affected by temperature and salinity (Kennedy et al, 2002), this type of noble gas can be qualitatively distinguished by modelling their solubility features in air-saturated water. For crustal-derived radiogenic noble gases, their contents can be calculated from the radiogenic element content of the crust (Ballentine et al, 2002; Kennedy et al, 2002). Mantle-derived noble gases can be identified from their specific contents and isotopic ratios such as $^{3}He/^{4}He$, combined with the geologic setting of the study area such as the existence of deep-seated faults.

Because of the scarcity and chemical inertness of noble gases, and the diversity and discriminability of various sources of noble gases, they are widely used in such applications as the study of natural gas genesis (Xu, 1998; Porcelli and Ballentine, 2002; Dai et al, 2008; Liao et al, 2012; Hunt et al, 2012), calculation of terrestrial heat flow (Polyak et al, 1985; Zhang et al, 2003; Liu et al, 2007b), dating of source rock (Liu and Xu, 1993; Liu et al, 2010; Tao et al, 2012), division of structural zones (Oxburgh and O'Nions, 1987; Xu et al, 2003; Ding et al, 2005; Liu et al, 2007b), tracing of oil and gas migration (Prinzhofer et al, 2000; Fan, 2001; Liu et al, 2001; Liu et al, 2007a), and deep

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fluid analysis (Craig et al, 1978; Xu et al, 1989; Ballentine et al, 2002). In the above applications, the tracing of oil and gas migration, which has made significant progress in noble gas research in recent years, is based mainly on the isotope separation and fractionation of noble gases. Isotope separation during noble gas migration alters the ratio of light to heavy noble gases, which can be used for identifying oil and gas migration. Prinzhofer et al (2000) and Fan (2001) both reported that $^{4}He/^{40}Ar$ and $^{20}Ne/^{36}Ar$ ratios could be used to trace oil and gas migration. Isotope fractionation occurring during the process of noble gas migration determines the final isotope value of noble gases, thus they also can be used for tracing oil and gas migration. Liu et al (2007a) proposed that the $^{3}He/^{4}He$ ratio can be used to trace oil and gas migration. Moreover, Prinzhofer et al (2000) and Liu et al (2007a) combined existing natural gas migration indices to confirm the dependability of noble gases in tracing oil and gas migration.

A large number of investigations have been conducted on the application of noble gases of the Sichuan Basin (Xu et al, 1989; Zhang, 1992; Liu and Xu, 1992; Liu et al, 2007b). However, the study of noble gases of the middle part of the western Sichuan Depression is rarely reported (Fan, 2001). Further investigation of the natural gas features and migration processes of this region requires analysis of the geochemical characteristics of noble gases contained in natural gas. In this paper, based on the geochemical characteristics of noble gases contained in Xujiahe and Jurassic natural gases from the middle part of the western Sichuan Depression, qualitative and quantitative analysis was undertaken for the study of the source of noble gases and for estimating the terrestrial heat flow. Further, isotopes of noble gases are used for tracking gas sources and natural gas migration.

2 Geological background

The western Sichuan Depression is a deep morphologic area of continental basins in the western region of the Sichuan basin that formed after the Upper Triassic. It is the foreland basin of the Longmen Mountain nappe structural belts. The western Sichuan Depression in enclosed by the Longmen Mountain nappe structural belts in the west, by the Longquan Mountain nappe structural belts in the east, by the Micang Mountain nappe structural belts in the north and by the Emei-Washan fault block in the south. The development of the Longmen Mountain thrusting nappe structure in the Indosinian orogeny resulted in a gradual exit of the paleo Tethyan Sea from the Sichuan basin to form the western Sichuan Depression. Later, successive deposits of the marine Ma'antang and Xiaotangzi formations, and the terrestrial Xujiahe, Jurassic and Cretaceous formations occurred in the western Sichuan Depression (Zheng et al, 2007). The marine Ma'antang and Xiaotangzi formations and the terrestrial Xujiahe formation are important source rocks, and the terrestrial Xujiahe, Jurassic and Cretaceous clastic formations are important reservoirs in the western Sichuan Depression. The Xiaoquan–Fenggu structure belts in the middle part of the western Sichuan Depression are located in the Mianzhu–Yanting uplift, which lies east-northeast (ENE) and includes the Xaoquan, Xingchang, Hexingchang, Gaomiaozi and Fenggu gas-bearing subsidiary structure units from west to east (Fig. 1). This region, which comprises the present study area, contains sets of effective source rocks and reservoirs. Favorable source-reservoir-caprock assemblages developed abundant natural gas resources, particularly the Xiaoquan, Xinchang, Hexingchang and Fenggu gas fields. The natural gas in the study area is mainly coal-related, with a high dryness index ($C_1/(C_1–C_5)$, in volume), a high maturity, and a

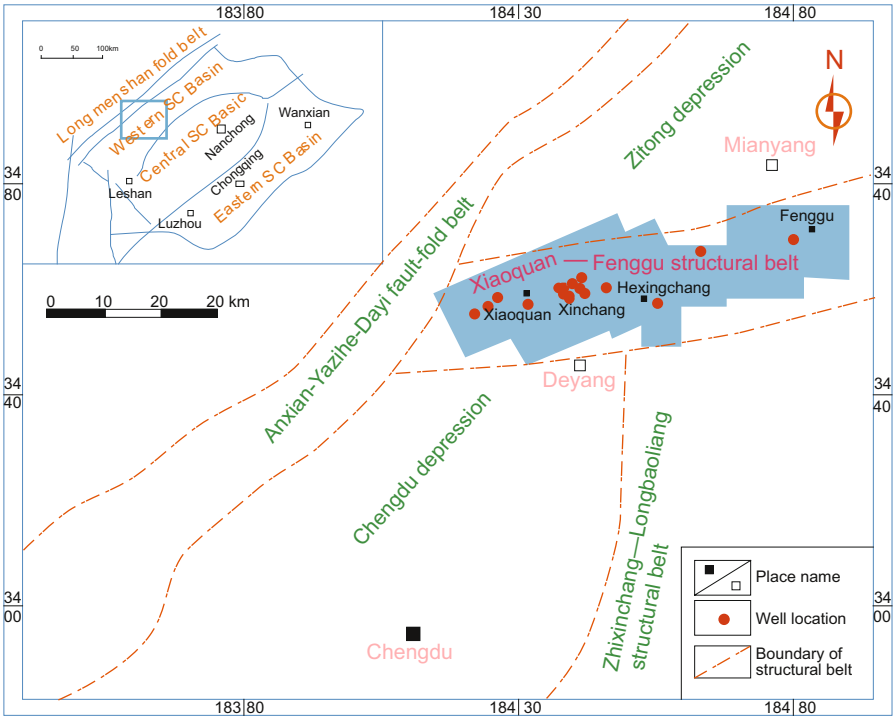

Fig. 1 Main tectonic units and locations of sampling sites in the middle part of the western Sichuan Depression, China

complex relationship with its source (Shen et al, 2011).

To study the characteristics of noble gases in the natural gas and to trace natural gas migration in the study region, 12 samples were collected and a series of analyses and tests was conducted on them.

3 Collection and analysis of samples

Twelve natural gas samples were collected from the second member of the Xujiahe formation (T_3x^2), the fourth member of the Xujiahe formation (T_3x^4), the Baitianba formation of the Lower Jurassic (J_1b), the Qianfoyan formation of the Middle Jurassic (J_2q), the Shaximiao formation of the Middle Jurassic (J_2s) and the Penglaizhen formation of the Upper Jurassic (J_3p) of the Xiaoquan, Xinchang, Hexingchang and Fenggu gas reservoirs (Table 1) in the west Sichuan Depression. To prevent contamination, all the samples were collected from individual layer production wells, and most were obtained from areas of high gas to water ratios of >95%. Due to the effect of gas-water separation in the natural gas production process, the noble gas isotopes generally reflect the gas-water separation in the wellbore during the production process rather than that during the geological process. Because the noble gases in natural gas from production wells with high gas to water ratios are almost completely separated to the gas phase, such gas–water separation effects can be neglected.

The 12 natural gas samples were analysed to determine the noble gas abundances and isotopes by the Lanzhou Center for Oil and Gas Resources, Institute of Geology and Geophysics, Chinese Academy of Sciences (CAS) using an MM5400 mass spectrometer (Micromass UK Ltd.). The test methods and processes have been reported elsewhere (Ye et al, 2001; 2007). Partial analysis results are shown in Table 1.

4 Results

From the results of this study and of 7 natural gas samples detailed by Fan (2001) (see Table 1), the main noble gases in the middle part of western Sichuan Depression are determined to be light noble elements of He, Ne and Ar.

4.1 He

The $^4He/^{20}Ne$ ratios (878-13800) of the 12 tested natural gas samples were significantly higher than that (0.318) of atmosphere-derived noble gases, indicating that contamination of the natural gas samples by air was negligible throughout the process of collection, storage and analysis (Kotarba and Nagao, 2008). The natural gas samples have low $^3He/^4He$ ratios (0.014×10^{-6}-0.069×10^{-6}) (Table 1). The $^3He/^4He$ ratio of a natural gas higher than the atmospheric average $^3He/^4He$ ratio of 1.4×10^{-6} generally indicates that the natural gas has mixed with mantle-derived He (Xu, 1998). The $^3He/^4He$ ratios of the tested natural gas samples were

Table 1 Partial analysis results of noble gas isotope in natural gas samples obtained from the middle part of western Sichuan Depression, China

No.	Well	Stratum	Depth m	$^3He/^4He$ ($\times10^{-6}$)	$^4He/^{20}Ne$	$^4He/^{40}Ar$	$^{40}Ar/^{36}Ar$	From
1	Chuanxiao 163-2	J_3p	677.75	0.0143	3451	9.97	327	This work
2	Xiaosui 1	J_2s	1833.64	0.0151	5573	9.66	397	
3	Xin 806	J_2q	—	0.0199	7282	10.42	377	
4	Chuanxiao 455	J_1b	2297.00	0.0203	2577	7.85	352	
5	Xin 22	T_3x^4	3884.01	0.0206	878	6.34	360	
6	Xin 101	T_3x^4	—	0.0248	1618	6.04	342	
7	Lian 116	T_3x^4	3959.90	0.0299	2602	6.95	405	
8	Chuanfeng 563	T_3x^4	3742.50	0.0304	1254	6.57	343	
9	Xin 856	T_3x^2	4592.00	0.0343	2783	6.69	427	
10	Xin 10	T_3x^2	4908.00	0.0428	1350	8.99	471	
11	Chuanhe 127	T_3x^2	4581.50	0.0434	1595	5.94	491	
12	Chuangao 561	T_3x^2	4958.00	0.0556	13800	1.80	424	
13	Chuanxiao 136	J_3	650.00	0.0332	—	29.62	372	(Fan, 2001)
14	Chuanxiao 134	J_3	1710.00	0.0241	—	10.02	739	
15	Chuanxiao 129	J_2	2356.00	0.0227	—	6.33	545	
16	Chuanxiao 152	J_2	2730.00	0.0322	—	4.69	465	
17	Chuanxiao 135	J_1	2752.00	0.033	—	5.01	676	
18	Chuanxiao 96	T_3	2628.00	0.0693	—	3.24	448	
19	Chuanhe 127	T_3	4566.00	0.0201	—	7.53	492	

Notes: Short line (—) indicates missing data.

less than the atmospheric average ratio, indicating that the noble gases in this study area are of mainly crustal origin. Noble gases from various sources exhibit distinctive $^{3}He/^{4}He$ end-member values (Ozima and Podosek, 2002; Kotarba and Nagao, 2008), such as $^{3}He/^{4}He$ ratios of 1.4×10^{-6}, 12×10^{-6} and 0.01×10^{-6} for atmospheric, mantle and crustal sources, respectively. The relationship of $^{3}He/^{4}He$ ratios of the samples with the three $^{3}He/^{4}He$ end-member values of atmospheric, mantle and crustal sources can be used for qualitatively determining the noble gas source. As shown in Fig. 2, the $^{3}He/^{4}He$ ratios of the 12 samples in the study area were concentrated on the lower right-hand corner, close to the crustal end-member values, indicating an obvious crustal origin.

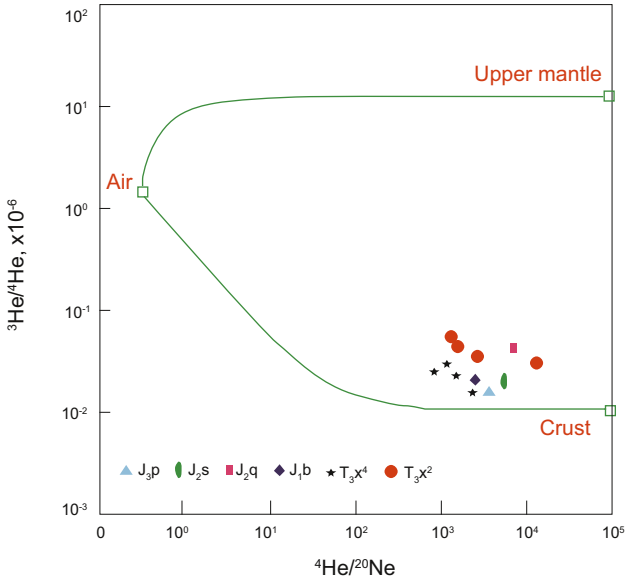

Fig. 2 Classification of noble gas origin by $^{3}He/^{4}He$ versus $^{4}He/^{20}Ne$ ratios (modified according to Kotarba and Nagao, 2008)

4.2 Ne

^{21}Ne and ^{22}Ne are generally derived from the nucleogenic products of O, F, and Mg elements or deep mantle-derived material (Ballentine et al, 2002). Because these isotopes were not detected in the tested natural gas samples, the noble gases in the study area are probably of crustal origin. Little ^{20}Ne is produced in the decay process of crustal elements; therefore, if this isotope is not provided by magma, it is likely derived from the atmosphere (Xu, 1998; Ballentine et al, 2002). The abundance of ^{20}Ne in the test samples is 0.0032-0.74 ppm, which is substantially less than the 16.5 ppm of ^{20}Ne of atmosphere-derived noble gases. The $^{4}He/^{20}Ne$ ratios (878-13,800) of the samples are significantly higher than that (0.318) of the atmosphere-derived noble gas (Ozima and Podosek, 2002).

The low ^{20}Ne abundance and high $^{4}He/^{20}Ne$ ratio of the natural gas samples in the study area may be the result of hydrocarbon gases and crustal-derived noble gases being mixed and diluting the atmosphere-derived compositions. Such mixing inevitably dilutes the atmosphere-derived noble gases and results in a lower abundance of ^{20}Ne in gas reservoirs than those in the atmosphere. Crustal-derived noble gases with a high abundance of ^{4}He mixed with atmosphere-derived noble gases may have resulted in higher $^{4}He/^{20}Ne$ ratios of the natural gas samples than that of the atmosphere.

4.3 Ar

Of the three noble gases sources, atmosphere-derived noble gases exhibit the lowest $^{40}Ar/^{36}Ar$ ratio (Xu, 1998). The $^{40}Ar/^{36}Ar$ ratios (324-691) of the natural gas samples are all significantly larger than that (296) of the atmosphere (Ozima and Podosek, 2002). These results indicate that the atmosphere-derived Ar content is low in the samples and Ar is mostly derived from crustal radioactive or deep-mantle materials. Although crustal-derived and mantle-derived noble gases both exhibited high $^{40}Ar/^{36}Ar$ ratios, He and Ne isotope analysis indicates that the noble gases of the natural gas samples are of crustal origin. Therefore, the high $^{40}Ar/^{36}Ar$ ratios of natural gas from the middle part of the western Sichuan Depression are mainly from crustal radiogenic Ar.

5 Discussion

5.1 Quantitative contributions of atmosphere, crust and mantle sources to noble gases

As shown in Fig. 2, the noble gases in the study area are mostly of crustal origin with little contribution from atmosphere and mantel sources. The proportion of noble gases from the latter two sources is low in the study area's samples and their volume percentages and relative contribution is rarely reported. However, because these issues are relevant to the analysis of natural gas genesis, such quantitative research is useful. Therefore, in the present study, the contributions of noble gases of the three origins (atmosphere, crust and mantle sources), were quantitatively calculated and the natural gas genesis was investigated.

Many scholars have reported that the contribution of noble gases derived from the atmosphere is negligible in natural gas. Thus, most quantitative calculations consider crustal-derived and mantle-derived noble gases in binary mixed models (Xu, 1998; Xu et al, 2003). However, recent studies have demonstrated that atmosphere-derived noble gases are also important contributors to the total composition of noble gases (Kennedy and Torgersen, 2002; Zhou et al, 2005). The volume percentages of He from various sources against total He are generally used to determine the contribution of noble gases of various origins. The volume percentage of atmosphere-derived He can be determined after obtaining the air-corrected values of total He ($(^{3}He/^{4}He)_C$), which is defined as the sum of crust and mantle He. According to the air-corrected He and measured He, it is easy to calculate the contribution of atmosphere-derived He. The air-corrected He ($(^{3}He/^{4}He)_C$) is expressed as (Craig et al, 1978; Ballentine et al, 2002)

$$(^{3}He/^{4}He)_c = \frac{(^{3}He/^{4}He)_s \times (^{4}He/^{20}Ne)_s/(^{4}He/^{20}Ne)_{air} - (^{3}He/^{4}He)_{air}}{(^{4}He/^{20}Ne)_s/(^{4}He/^{20}Ne)_{air} - 1} \quad (1)$$

where subscripts c, s and air refer to the corrected, measured and air-derived ratios, respectively. The quantitatively calculated air-corrected $^{3}He/^{4}He$ ratios are from 1.41×10^{-8} to

5.53×10^{-8}. According to the corrected and measured $^3He/^4He$ ratios, the volume percentage of atmospheric He against total He is obtained as 0.11%-2.01% (Fig. 3).

After determining the atmosphere-derived He, the contribution of mantle-derived He can be calculated with the following binary mixed model (Xu, 1998):

$$\%He_{mantle} = 100\times(R - R_c)/(R_m - R_c) \quad (2)$$

where R is the air-corrected $^3He/^4He$ ratio, and R_m and R_c are mantle-derived and crustal-derived $^3He/^4He$ ratios of 12×10^{-6} and 0.01×10^{-6}, respectively. The volume percentage of mantle-derived He obtained by quantitative calculation against total He is 0.03%-0.38% (Fig. 3).

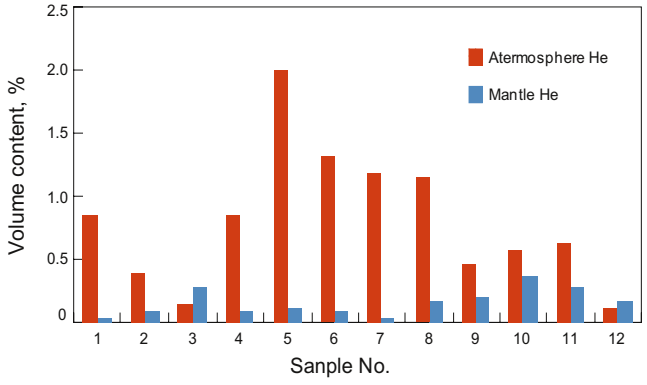

Fig. 3 Volume percentage of atmosphere-derived and mantle-derived He against the total He content

After obtaining the contents of atmosphere-derived and mantle-derived He, the volume percentage of crustal-derived He obtained by quantitative calculation against total He is 97.9%-99.7%. This result demonstrates the high contribution of crustal-derived He. Hence, the contribution of crustal-derived noble gases is far greater than those of atmospheric and mantle origins. Fig. 3 indicates that with the exception of two natural gas samples, Nos. 3 and 12, which exhibited the least atmosphere-derived noble gas contribution, the contents of atmosphere-derived noble gases were higher than mantle-derived noble gases for the other samples. Thus atmosphere-derived noble gases make some contribution to the total noble gases in the natural gas samples; the volume percentage of atmosphere-derived He against the total He for one-third of the natural gas samples is 1%-2%. However, this contribution is negligible in comparison with the volume percentage of crustal-derived noble gases of 97.9%-99.7%. Moreover, the contribution of mantle-derived noble gases in all the natural gas samples is low with a maximum volume percentage of only 0.38%. The quantitative analysis of the contributions of the three sources of noble gases reveal that the noble gases in study area are derived mainly from the crust and the structure is stable with a lack of deep faults to facilitate the migration of mantle-derived noble gases, and that the natural gases in the study area are crustal biotic gases without any admixture of mantle-derived abiotic hydrocarbons.

5.2 He isotopes and terrestrial heat flow

Terrestrial heat flow is a significant parameter in oil and gas geology and is closely related to the evolution of source rock, the maturity of organic matter and the hydrocarbon generation threshold of oil and gas. The higher terrestrial heat flow values mean the faster the thermal evolution of organic matter, the lower the hydrocarbon generation threshold and the more favourable the hydrocarbon generation and expulsion (Xu, 1994). Because the terrestrial heat flow is mostly derived from crustal radiogenic heat and mantle heat, the He of natural gas in main hydrocarbon reservoirs is of crust- and mantle-derived. Thus, the terrestrial heat flow and $^3He/^4He$ ratios are both associated with crustal radiogenic elements and mantle energy. Therefore, a correlation exists between He isotopes of natural gas in hydrocarbon reservoirs and terrestrial heat flow. This relationship can be expressed as (Polyak et al, 1985)

$$Q = 6.993\ln(^3He/^4He) + 165.16 \quad (3)$$

where Q is the terrestrial heat flow. The terrestrial heat flow in the study area obtained using Eq. (3) is in the range of 39-50 mW/m^2 with an average value of 44 mW/m^2, very close to previously reported value of 32-47 mW/m^2 with an average of 42 mW/m^2 for the Sichuan Basin (Xu et al, 1998). This demonstrates that the calculated result is reliable and the noble gas method is an effective way to obtain the terrestrial heat flow in the study area.

5.3 $^{40}Ar/^{36}Ar$ ratio variation and natural gas source

In previous analysis of K and Ar characteristics, Liu and Xu (1987) found that the Ar in natural gas is mostly derived from source rock and that the decayed product of ^{40}K in source rock is the main source of radioactive ^{40}Ar in natural gas. With increasing source rock ages, radiogenic ^{40}Ar increases in the source rock; thus $^{40}Ar/^{36}Ar$ ratio also increases. Therefore, gas generation from young (old) source rocks into gas reservoir will result in lower (higher) $^{40}A/^{36}Ar$ ratios, which is described as the ^{40}Ar time-accumulating effect of source rocks. This effect is a characteristic of crustal-derived natural gases from stable areas of source rocks without being mixed with mantle-derived gases (Xu et al, 2003). Qualitative and quantitative analysis have confirmed that the natural gas in the study area is of mainly crustal origin; therefore, the aging effect of source rocks can be used to study gas and source rock correlation. In the present study, the ^{40}Ar time-accumulating effect of source rocks is used to study the gas–source rock relationship in the study area, and confirmed by using the correlation of light hydrocarbon gases and source rocks.

As shown in Fig. 4, the 12 tested samples are divided into three categories, A, B and C, according to their $^{40}Ar/^{36}Ar$ and ^{40}Ar content.

In category A, all the samples were collected from the T_3x^2 reservoir. These samples have relatively high $^{40}Ar/^{36}Ar$ ratios and ^{40}Ar contents because the T_3x^2 natural gas samples were older than those of other samples; thus the ^{40}Ar time-accumulating effect of source rocks was more significant. Considering the concentrated distribution of T_3x^2 samples, and their higher Ar isotope ratios and ^{40}Ar content, combined with the ^{40}Ar time-accumulating effect of source rocks, it can be

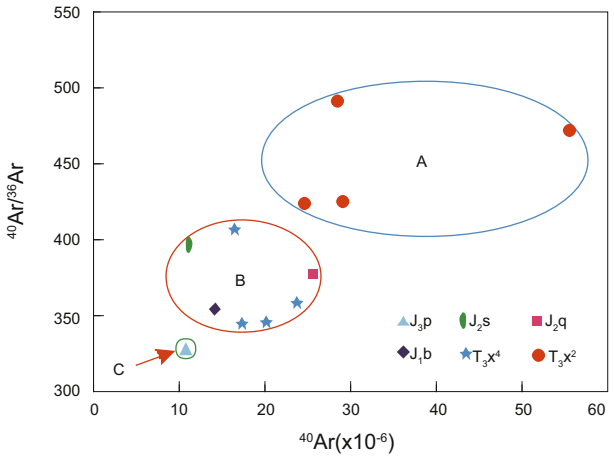

Fig. 4 Relationship between $^{40}Ar/^{36}Ar$ ratio and ^{40}Ar content in the tested samples

concluded that the T_3x^2 natural gas samples are derived from the same source rock and the source rock is older than that of the other natural gas samples. Previous research demonstrates that the natural gas from the Xujiahe formation of the Upper Triassic to Cretaceous reservoir was derived predominantly from Upper Triassic terrestrial source rock, because the T_3x^2 source rock is the oldest of the Upper Triassic terrestrial source rocks (Cai and Miao, 2000; Zhu et al, 2006; Shen et al, 2011). Considering the aging effect of ^{40}Ar of source rocks, T_3x^2 natural gas should be derived from T_3x^2 source rock, which is consistent with a previously reported theory of T_3x^2 natural samples being self-generating and self-preserving (Shen et al, 2011).

The samples in category B were derived from the T_3x^4, J_1b, J_2q and J_2s reservoirs. The $^{40}Ar/^{36}Ar$ ratios and ^{40}Ar contents of these samples were lower than those in the category A samples. Samples from J_1b, J_2q and J_2s exhibit similar distribution characteristics and $^{40}Ar/^{36}Ar$ ratios to those of T_3x^4. Therefore, considering the ^{40}Ar time-accumulating effect of source rocks, natural gas samples from J_1b, J_2q, J_2s and T_3x^4 are derived from the same source rock, which is younger than the T_3x^2 source rock. Previous research demonstrates that Xujiahe formation source rock in the western Sichuan depression is more developed, of which T_3x^3 and T_3x^5 formations have developed favorable source rocks; T_3x^2 and T_3x^4 formations are significant reservoirs in the study area, they also developed source rock and have made significant contributions to the natural gas of the study area (Zhu et al, 2006; Shen et al, 2011). Therefore, the category B samples are derived from one or more parts of the T_3x^3, T_3x^4 and T_3x^5 source rocks above the T_3x^2 source rock. The maximum $^{40}Ar/^{36}Ar$ ratios and the highest ^{40}Ar contents of the category B samples are very close to the corresponding minimum values in the category A samples. According to the ^{40}Ar time-accumulating effect of source rocks, and the source rock distribution characteristics in the study area that the T_3x^3 formation above the T_3x^2 formation developed favorable source rock, it can be concluded that T_3x^3 source rock has contributed to natural gas in category B. The T_3x^4 formation also developed source rock, which supplied natural gas to the T_3x^4 gas reservoir. The Jurassic natural gas is derived predominantly from the underlying Xujiahe formation source rock, and the main migration was upward (Shen et al, 2011). The T_3x^5 source rock below the Jurassic formation is a favorable source rock in the study area. Hydrocarbons were generated from this source rock and migrated; so the Jurassic natural gas has a contribution from the T_3x^5 source rock. The ^{40}Ar time-accumulating effect of source rocks indicates that the T_3x^4 and Jurassic samples in the category B samples were derived from the same source rock; thus, the T_3x^4 natural gas has been derived from the T_3x^5 source rock. These results demonstrate that the T_3x^4, J_1b, J_2q and J_2s natural gas in the study area are supplied by T_3x^3, T_3x^4 and T_3x^5 source rocks. In addition, the common contributions of radioactive Ar from the three source rocks result in T_3x^4 natural gas having similar $^{40}Ar/^{36}Ar$ ratios to J_1b, J_2q and J_2s natural gas.

The only sample in category C was from the J_3p reservoir, and its $^{40}Ar/^{36}Ar$ ratio and ^{40}Ar content are minimal. According to the ^{40}Ar time-accumulating effect of source rocks, this J_3p sample should have been derived from younger source rock. From this, combined with previous research on the origin of Jurassic natural gas (Shen et al, 2011), it can concluded that the Jurassic source rock is most likely the source of J_3p natural gas.

Characteristic parameters of light hydrocarbons are commonly used to investigate gas–source rock relationships (Cai and Miao, 2000; Shen et al, 2011). In the present study, the light hydrocarbon, extracted from T_3x^2, T_3x^3, T_3x^4 and T_3x^5 source rocks and from T_3x^2, T_3x^4 and Jurassic natural gas, is used to examine the gas and source rock relationship and study the reliability of noble gas as an indicator of the source of natural gas. The results show that the light hydrocarbon characteristic parameters of T_3x^2 natural gas have a strong correlation with the T_3x^2 source rock, indicating that the T_3x^2 gas reservoir is self-generating and self-preserving one (Shen et al, 2011). Five pairs of light hydrocarbon parameters including isohexane/*n*-hexane(iC_6/nC_6), methylcyclohexane/*n*-heptane(MCC_6/nC_7), methylhexane/*n*-heptane(MC_6/nC_7), 2-methylpentane/3-methylpentane(2-MC_5/3-MC_5), cyclopentane/2,3-Dimethylbutane(CC_5/2,3-DMC_4) ratios were used to trace the source of T_3x^4 and Jurassic natural gases. As shown in Fig. 5, only the MCC_6/nC_7 ratios of light hydrocarbons from T_3x^3 and T_3x^4 source rock are different from that of T_3x^4 and Jurassic natural gas; the other four parameters show a strong correlation between the source rock and natural gas. The similarity of the five pairs of parameters was substantial between T_3x^4 and Jurassic natural gas; in

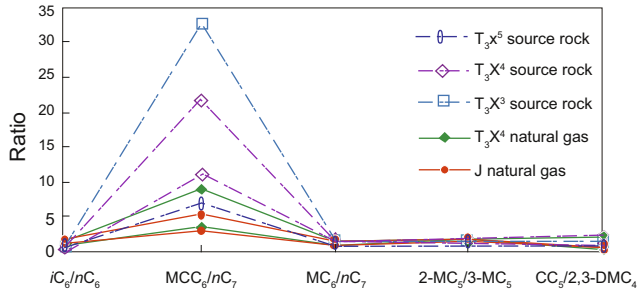

Fig. 5 Comparison of source rock and natural gas in the middle part of the western Sichuan Depression

addition, these parameters of T_3x^4 and Jurassic natural gas also show strong correlation with T_3x^4 and T_3x^5 source rock, indicating that the contributions of T_3x^4 and T_3x^5 source rock to T_3x^4 and Jurassic natural gas are significant. The good correlation of the characteristic parameters of light hydrocarbons between source rock and natural gas confirms that T_3x^3, T_3x^4 and T_3x^5 source rock have provided natural gas for T_3x^4 and the Jurassic reservoir (Fig. 5). This result is consistent with that by using the ^{40}Ar time-accumulating effect of source rocks, which demonstrates that the ^{40}Ar time-accumulating effect of source rocks for gas–source research is feasible in the study area.

5.4 $^4He/^{40}Ar$ ratio variation and natural gas migration

The $^4He/^{40}Ar$ ratios of these natural gas samples are 1.80-29.62, and the majority of the samples ranged from 4.68 to 10.02. With the exception of T_3x^2 ,T_3x^4 and the Jurassic reservoir, which each has a $^4He/^{40}Ar$ ratio below that of the crust average of 5 (Ballentine and Burnard, 2002) , the $^4He/^{40}Ar$ ratios of other samples are higher than that of the crustal average (Fig. 6; Table 1). Such a result can be attributed to preferential ^4He release. Noble gases undergo two main processes from production to final position (Ballentine and Burnard, 2002), which include 1) the release of noble gases from minerals through recoil, diffusion, fracturing and chemical transformation, and 2) migration to current locations from the production site. During the first process, diffusion, dilatant fracturing and varied closure temperatures of noble gas cause the $^4He/^{40}Ar$ ratios of natural gas to be higher than that of the crustal average (Lippolt and Weigel, 1998; McDougall and Harrison, 1998; Ballentine and Burnard, 2002). Under such conditions, the diffusivity of ^4He is significantly higher than that of ^{40}Ar in the same mineral, resulting in ^4He forming a diffusion gradient. In addition, noble gases liberated from minerals during the dilatant fracturing process, and more He than Ar was lost at any given dilatancy (Ballentine and Burnard, 2002). Moreover, the closure temperature of ^{40}Ar is generally higher than 200 °C; while that of ^4He is lower than 200 °C, which causes a preferential release of ^4He (Ballentine and Burnard, 2002). These factors all contribute to the preferential release of ^4He, which causes the $^4He/^{40}Ar$ ratios in most of the natural gas samples to exceed that of the crustal average.

During the second process, the atomic weight difference of different noble gases in natural gas causes faster migration of lighter noble gases, leading to a gradual separation of light and heavy noble gases during the migration process. Under such conditions, light/heavy noble gas ratios such as $^4He/^{40}Ar$ and $^{20}Ne/^{36}Ar$ increase along the transport direction, namely the separation characteristic of light and heavy noble gas, which can be used for tracing of natural gas migration (Fan, 2001). Prinzhofer et al (2000) have conducted an analysis of carbon isotopes, light hydrocarbons and noble gas to trace hydrocarbon migration, and found that the conclusion for oil/gas migration obtained by using noble gas is accordance with that by using the other two methods, confirming the feasibility of using noble gas separation characteristics to trace hydrocarbon migration. As shown in Fig. 6, the $^4He/^{40}Ar$ ratios of T_3x^2 and T_3x^4 natural gas samples from the study area showed a concentrated distribution, which may be related to the characteristic of source-reservoir assemblage of the two layers. The analysis mentioned above shows that the T_3x^2 gas reservoir is self-generating and self-preserving and that T_3x^4 natural gas is derived mainly from T_3x^3, T_3x^4 and T_3x^5 source rocks. Because the migration distance of natural gas from these two layers is short, ^4He and ^{40}Ar are not significantly separated and $^4He/^{40}Ar$ ratios display a concentrated distribution. Jurassic natural gas is mostly derived from the underlying Xujiahe source rocks with a relatively long migration distance. For the J_1 and J_2 natural gas, there is no significant relationship of $^4He/^{40}Ar$ ratios between them (Fig. 6), it probably due to the lower thickness of J_1 formation (<300 m), the natural gas migration distance from J_1 to J_2 formation is short, so the ^4He and ^{40}Ar separation is not significant during the natural gas migration process. The $^4He/^{40}Ar$ ratios of J_3 natural gas are higher than those of the J_2 samples (Fig. 6). This is probably mainly due to the larger thickness of the J_2 formation (average thickness about 1000 m). Hence, the natural gas migration distance from the J_2 to the J_3 formation is long, so the ^4He and ^{40}Ar separation is significant and the difference of $^4He/^{40}Ar$ between J_2 and J_3 natural gas illustrate that natural gas migrates from the former to the latter. From these results, the following conclusions can be drawn: 1) when the migration distance of natural gas is short, ^4He and ^{40}Ar separation is not significant, and the $^4He/^{40}Ar$ ratio fluctuation is small; therefore, the $^4He/^{40}Ar$ ratios cannot be used to estimate the natural gas migration distance; 2) when the natural gas migration distance is long, ^4He and ^{40}Ar separation is significant, and the $^4He/^{40}Ar$ ratios increase with migration distance; hence, the variation trends of $^4He/^{40}Ar$ ratios can indicate the natural gas migration.

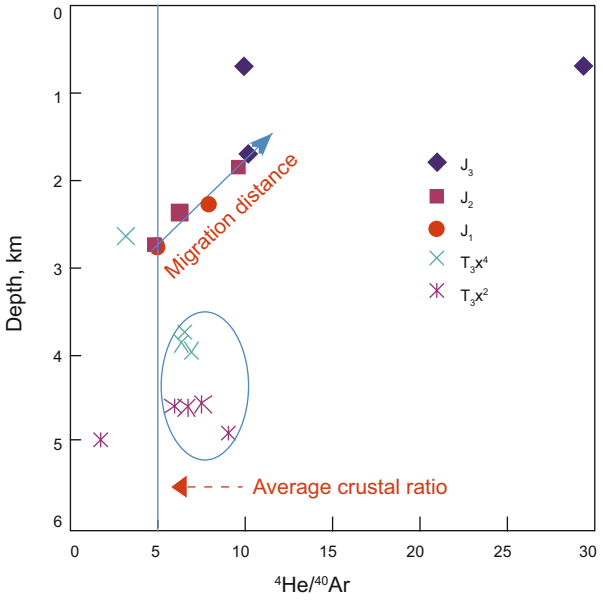

Fig. 6 Relationship between $^4He/^{40}Ar$ ratios and depth

5.5 Relationship of $^4He/^3He$ ratios, $\delta^{13}C_1$ and natural gas migration

In recent years, many studies worldwide have focused on the relationship between noble gases and carbon isotopes,

the results of which indicate that noble gases and $\delta^{13}C_1$ in hydrocarbons, rocks and mantle fluid are closely related. Effective application of these relationships has led to achievements in respective research areas (Liu and Xu, 1997; Hulston et al, 2001; Mata et al, 2010). In natural gas research, $\delta^{13}C_1$ has been widely applied in such areas as classification of natural gas genetic type, maturity analysis, migration research and gas–source correlation. The noble gases isotope ratios and contents of the same and different elements also provide abundant information on natural gas origin and migration. Noble gases and $\delta^{13}C_1$ share many characteristics, which play important roles in natural gas genesis and migration research (Dai et al, 2001; Prinzhofer et al, 2010; Liu et al, 2007).

Fig. 7 shows noble gas and $\delta^{13}C_1$ values of Xujiahe and Jurassic natural gas samples from the middle part of the western Sichuan Depression. The $^3He/^4He$ ratios and $\delta^{13}C_1$ values exhibit a good correlation that gradually decreased from the Xujiahe formation to the Jurassic formation. The noble gases in the middle part of the western Sichuan Depression are predominantly of crustal genesis. Crustal noble gases are derived mainly from the decay of radioactive elements such as U, Th and K. Because the content of these radioactive elements is higher in source rock than in the reservoir, the noble gas entering the gas reservoir is derived chiefly from source rock (Xu, 1998). For crustal noble gas, the variation of $^3He/^4He$ ratios depends on the ^4He content. When ^4He is released from minerals and migrates, the ^4He content increases and $^3He/^4He$ ratios decrease along the migration path. According to the principle of carbon isotope fractionation, $\delta^{13}C_1$ values decrease along the migration path. In the study area, $^3He/^4He$ ratios and $\delta^{13}C_1$ values of all the Jurassic natural gas samples are lower than those of the Xujiahe samples, and gradually decrease from the Xujiahe formation to the Jurassic layer, in addition, $^3He/^4He$ ratios and $\delta^{13}C_1$ values show a correlation, indicating an upward migration of natural gas from the Xujiahe formation to the Jurassic layer.

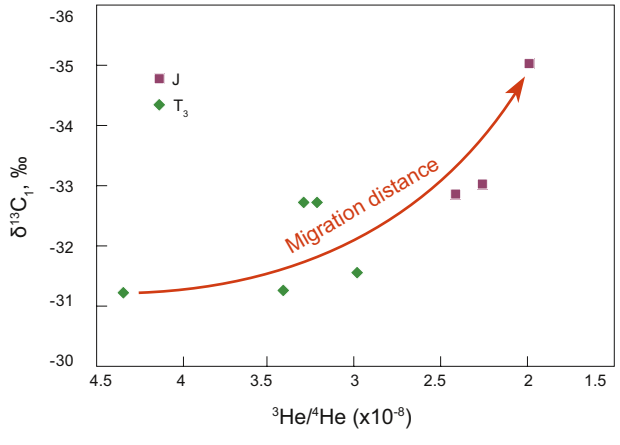

Fig. 7 Plot of $^4He/^{40}Ar$ ratio versus $\delta^{13}C_1$ value

6 Conclusions

In this paper, analysis was conducted on the geochemical characteristics of noble gases and their application in tracing natural gas migration in the gas reservoirs of the middle part of the western Sichuan Depression. The results are summarized in the following points:

1) Noble gases in natural gas in the middle part of the western Sichuan Depression are derived predominantly from the crust. The crustal genesis of noble gases indicates that the study area structure is stable and the natural gases were not combined with mantle-derived compositions.

2) The terrestrial heat flow in the study area was obtained, using noble gas isotopes, to be in the range of 39-50 mW/m^2 with an average value of 44 mW/m^2.

3) The study results from ^{40}Ar time-accumulating effect of source rocks indicate that in the study area, T_3x^2 natural gas is derived from T_3x^2 source rock; T_3x^4 and Jurassic natural gas are derived mainly from T_3x^3, T_3x^4 and T_3x^5 source rock; and a portion of Upper Jurassic natural gas may originate from Jurassic source rock.

4) The separation of ^4He and ^{40}Ar increases with natural gas migration distance. When the distance is longer, $^4He/^{40}Ar$ ratios can be used to indicate the migration distance of natural gas. When the migration distance is shorter, the separation of ^4He and ^{40}Ar is not significant; therefore, $^4He/^{40}Ar$ ratios cannot be used to indicate the migration distance. $^4He/^{40}Ar$ ratios of natural gas in the middle part of the western Sichuan Depression indicate an upward migration of natural gas in the Jurassic formations. $^3He/^4He$ ratios and $\delta^{13}C_1$ values show a decreasing trend from the Xujiahe formation to the Jurassic layer, which demonstrates that natural gases migrated from the former to the latter.

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