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Research paper

Differential fluid migration behaviour and tectonic movement in Lower Silurian and Lower Cambrian shale gas systems in China using isotope geochemistry

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A B S T R A C T

Isotope geochemistry has been introduced as a means to trace origin of the hydrocarbon and characterize highly productive shale gas systems recently. To assess the impact of tectonic movement and the sealing of shale gas systems, isotope geochemistry, pressure coefficients and the distribution of bitumens are analysed. Many samples yield isotope geochemical data with typical carbon isotopic reversals ($\delta^{13}C_1 > \delta^{13}C_2$) and hydrogen isotopic reversals ($\delta^{13}D_{C2H6} > \delta^{13}D_{CH4}$) in the Lower Silurian shale gas. Isotopically reversed gases are considered to originate in sealed, self-contained petroleum systems. Besides, isotope "reversals order" degree of shale gas has positive correlation with gas production. Isotopically normal gases from the Lower Cambrian indicate that this formation was a continued relatively open petroleum system when oil and gas generated. The pressure coefficients of the Lower Silurian shale gas reservoir range from 1.45 to 2.03, indicating that the reservoir is overpressurized, whereas the Lower Cambrian shale gas reservoir possesses a normal pressure system. Overpressurization of the Lower Silurian shale gas reservoir also indicates that it is a well-sealed system. The distribution and isotope geochemistry of bitumens in the Sinian dolomite and Cambrian shale suggests that the source rock of the Sinian hydrocarbon is the Cambrian shale. An unconformity induced from tectonic movement during the Tongwan period is interpreted to be the fluid migration tunnel and the cause of the differential shale gas content and production. Finally, the isotopic reversals associated with maturity, pressure coefficients and tectonic evolution can both assess the preservation conditions of the reservoir and explain the differential fluid migration behaviour.

1. Introduction

China has experienced a significant breakthrough in shale gas production in recent years. Sinopec stated that China produced more than 4.47 billion m^3 of shale gas in 2015 and that it will reach 20 billion m^3 in 2020 (data from Dr. Ma in the 8th International Symposium on Tight Sandstone and Shale Plays Exploration and Development). Most of the productive shales are found in the Lower Silurian Wufeng-Longmaxi shale and Lower Cambrian Qiongzhusi shale, Sichuan Basin, southwest China (Guo, 2016). However, the production and gas content of the Wufeng-Longmaxi shale are much greater than those of the Qiongzhusi shale (Zou et al., 2016).

Recently, isotope geochemistry has become a useful tool for shale gas exploration (Tilley and Muchlenbachs, 2013). The geochemical characteristics of shale gas and its utility for the shale gas industry have been discussed extensively (Martini et al., 2003; Zumberge et al., 2012; Wang et al., 2013). Numerous issues in shale gas systems can be examined with isotope geochemical data. Fluid and gas geochemical data are useful indicators in regional and

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tectonic studies (Yang, 2013). The major gas components (H_2O, CO_2, N_2, CH_4, S, and the halogens) and gas isotopes (of C, H, O, S, N, and the noble gases) are unique tracers that characterize the sources of gas and fluid samples and permit interpretation of their origin and migration behaviour (Yang et al., 2009). Wang et al. (2013) used carbon molecular moieties and isotopic data to trace the origins and migration process of natural gas in the northern Sichuan Basin. Zumberge et al. (2009) first observed and discussed isotopic reversal in gases within source-rock reservoir. Later, isotopic reversals were commonly considered restricted in sealed and self-contained system with mixing and accumulation of gases generated from diverse precursors (kerogen, retained oil and wet gas) at different thermal maturities (Hao et al., 2013; Xia et al., 2013; Curiale and Curtis, 2016). Furthermore, Tilley and Muchlenbachs (2013) used isotopic data and gas maturation levels to determine the relationship between high productivity shale and isotopic reversals, as well as trends of gas maturation in a sealed petroleum system. Additionally, the distribution of bitumens can indicate the presence of palaeo oil reservoirs as well as the pathways of hydrocarbon migration (Li et al., 2015). Therefore, isotope geochemistry, when associated with additional data, can be used to address diverse problems in shale gas systems and in other systems.

Source rock hydrocarbon generation, migration and accumulation are critically important in determining the present gas content of shale (Zhou et al., 2013). However, few studies have examined the differential gas content between the Cambrian and Silurian shale, nor have previous studies explained the poor gas content of the Cambrian shale. In this study, gas isotopic reversals, pressure coefficients and the geochemistry and distribution of bitumens in the Cambrian and Silurian shale gas reservoirs were used to identify the origin and migration of gas, to assess the sealing of the two shale gas systems and to examine the impact of tectonic movement in the Cambrian.

2. Geological setting

The Sichuan Basin is located to the east of the Tibetan Plateau, southwestern China (Fig. 1). The Sichuan Basin is in the transition zone between the Palaeo-Pacific Tectonic area and Tethys-Himalayan Tectonic area, bounded by the Longmen Mountains to the west, Micang and Daba Mountains to the north, Qiyue and Dalou Mountains to the east, and Daliang Mountains and Yunnan-Guizhou Plateau to the south (Liu et al., 2016). The tectonic evolution of the Sichuan Basin occurred in two stages: an earlier cratonic depression in the Palaeozoic and a later foreland basin stage in the Triassic (see Fig. 2).

The Sichuan Basin is a structurally complex, superimposed basin with prolific oil and gas production: it contains 106 gas fields and 14 oil fields. The largest shale gas fields (Fuling, Weiyuan, Changning) are found in the Sichuan Basin and the surrounding area, causing the Sichuan Basin to be regarded as the main productive shale gas area in China. Shale gas accumulations occur mainly in the Lower Cambrian Qiongzhusi shale formation (termed the Qiongzhusi Formation in most of the intrabasinal area but also called the Niutitang Formation along the basin's periphery) and the Lower Silurian Wufeng-Longmaxi shale formation. These two formations are mainly composed of marine, organic-rich shale with good shale gas potential. The primitive organic matter is dominated by amorphous macerals and belongs to type I and/or IIa kerogens (Dai et al., 2016). The equivalent vitrinite reflectance (EqVRo, %)

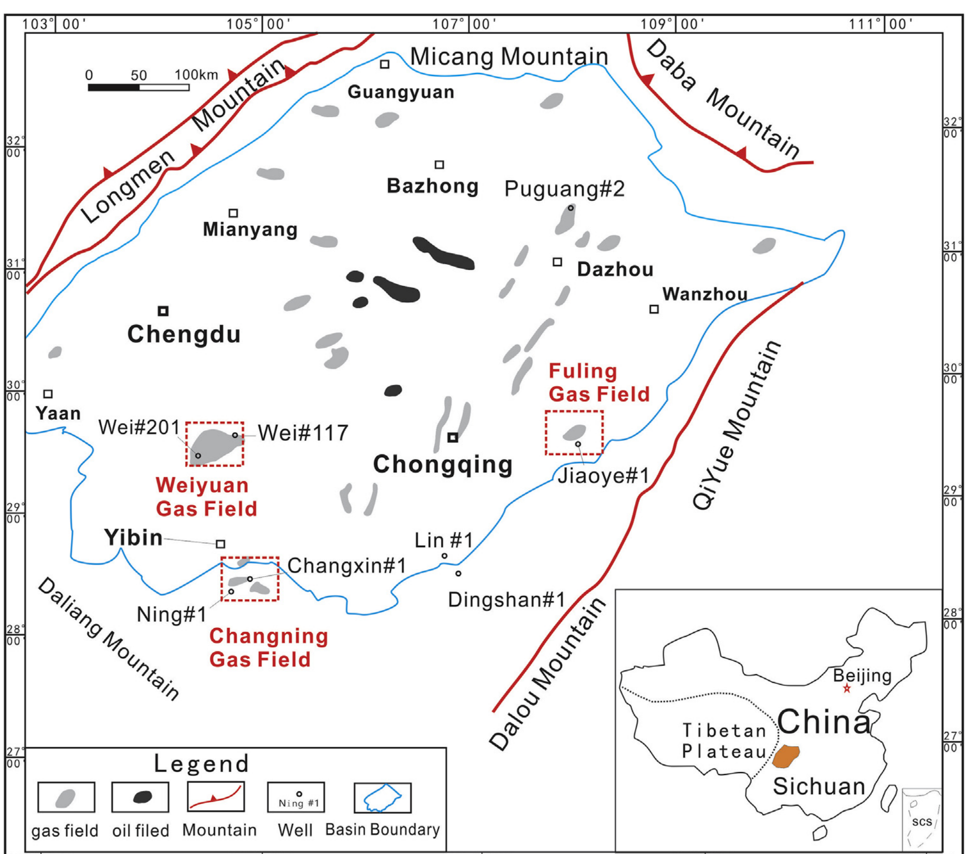

Fig. 1. Sketch map showing the structural outline of the Sichuan Basin and the location of major gas and oil fields.

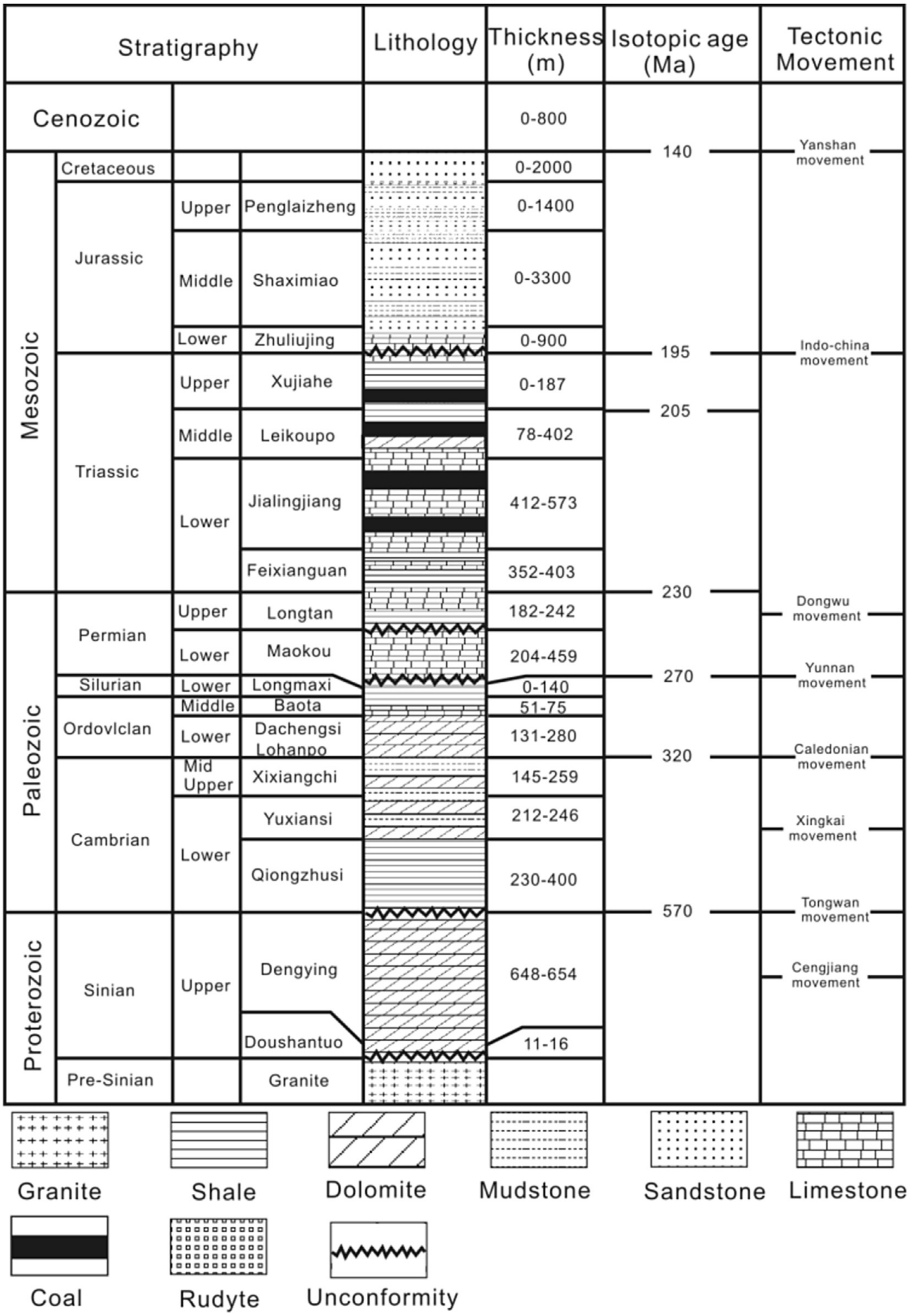

Fig. 2. Stratigraphic sequences in the Sichuan Basin.

values range from 1.8 to 3.8% in the Cambrian and Silurian shales (Zou et al., 2016; Guo, 2016), indicating that they are largely thermally over-mature and in a dry gas generation stage (Wang et al., 2013; Dai et al., 2016). However, these two sets of shales experienced multiple episodes of burial, uplift and erosion during the Mesozoic and Cenozoic, which decreased hydrocarbon preservation (Liu et al., 2012).

Intensive tectonic movement, such as that experienced during the Caledonian, Yanshanian, Indosinian, and Himalayan orogenies (Ma et al., 2004; Hao et al., 2013; Liu et al., 2016), can generate numerous faults and unconformity surfaces, which result in diverse hydrocarbon migration and gas preservation. The Upper Sinian

Dengying Formation consists of microcrystalline dolomite and contacts discordantly with the Lower Cambrian Qiongzhusi Formation. There is an unconformity between the Dengying Formation and the Qiongzhusi Formation. At the beginning of the Silurian, the Sichuan Basin experienced abundant sediment deposition. The Lower Silurian Longmaxi Formation is rich in organic matter. In the Yanshan period, two sets of shale experienced deep burial, and gas generation reached its peak. Then, repeated uplift and erosion resulted in hydrocarbon migration out of the formation (Guo, 2016). Additionally, an unconformity and faults induced by multiple tectonic movements greatly influenced the fluid migration and accumulation. The Lower Cambrian shale experienced greater Tongwan movement than the Lower Silurian shale, thus gas content and production differ between these two sets of shale. The shale gas production of the Silurian Longmaxi Formation is much greater than that of the Cambrian Qiongzhusi Formation (Fig. 3).

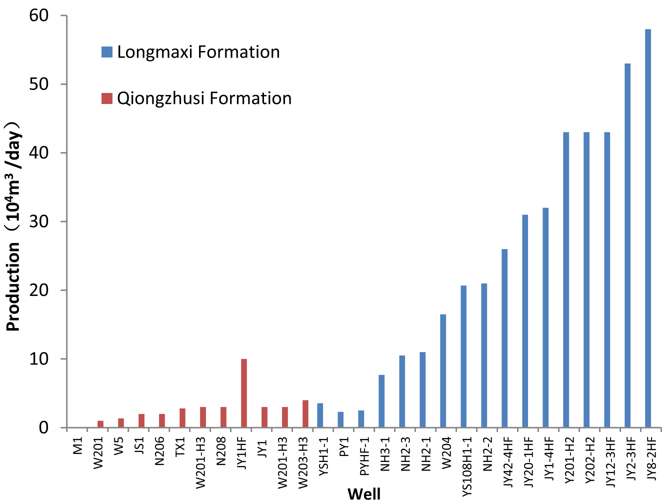

Fig. 3. Shale gas test production of the Longmaxi Formation and the Qiongzhusi Formation.

3. Geochemical characteristics of the shale gases

3.1. Composition of the Lower Paleozoic shale gas

Table 1 shows that alkanes are the dominant constituents of the Lower Paleozoic shale gas, of which methane is the most abundant. Methane content varies from 95.32 to 99.59%, with an average of 98.45%. The wetness of gas is 0.24%–0.78%, with an average of 0.58%. Propane content is only 0.01%–0.1%, and butane is absent. The Lower Paleozoic shale gas is therefore a typical dry gas. The non-hydrocarbon gases are found in low quantities, with concentrations of CO_2 varying from 0 to 1.74% and N_2 ranging from 0 to 4.05%.

In addition, previous studies determined that an $R/Ra > 0.1$

Table 1
Shale gas component and isotope properties inin Lower Silurian and Lower Cambrian (data sources: Wu et al., 2015; Dai et al., 2016 and this study).

Well	Age	Depth/m	EqVRo/%	Main component					Wetness /%	$\delta^{13}C$/(‰,VPDB)				δD/(‰,VSMOW)		$(^3He/^4He)/(\times 10^{-8})$	R/Ra	$(\delta^{13}C2-\delta^{13}C1)$/‰
				CH_4	C_2H_6	C_3H_8	CO_2	N_2		CH_4	C_2H_6	C_3H_8	CO_2	CH_4	C_2H_6			
Wei201	S	1520–1523	2.1	98.32	0.46	0.01	0.36	0.81	0.48	−36.9	−37.9			−140		3.594 ± 0.653	0.03	−1.0
Wei201-H1	S	2840		95.52	0.32	0.01	1.07	2.95	0.34	−35.1	−38.7			−144		3.648 ± 0.679	0.03	−3.6
Wei202	S	2595	2.4	99.27	0.68	0.02	0.02	0.01	0.70	−35.9	−42.8	−43.2	−2.2	−144	−164	2.726 ± 0.564	0.02	−5.9
Wei203	S	3137–3161	2.6	98.27	0.57		1.05	0.08	0.58	−35.7	−40.4		−1.2	−147				−4.7
Ning201-H1	S	2745		99.12	0.5	0.01	0.04	0.30	0.51	−27.0	−34.3			−148		2.307 ± 0.402	0.02	−7.3
Ning211	S	2313–1341	3.2	98.53	0.32	0.03	0.91	0.17	0.35	−28.4	−33.8	−36.2	−9.2	−148	−173	1.867 ± 0.453	0.03	−5.4
NingH2-1	S	2790		99.07	0.42	0.1	0	0.40	0.53	−28.7	−33.8	−35.4		−151	−156			−5.1
NingH2-2	S	2586		99.28	0.47	0.01	0	0.23	0.48	−28.9	−34			−149	−161			−5.7
NingH2-3	S	2503		98.62	0.42	0.01	0.59	0.37	0.43	−31.3	−34.2	−35.5		−151	−161			−2.9
NingH2-4	S	2568		99.15	0.44	0.01	0	0.40	0.45	−28.4	−33.8			−148	−169			−5.4
JY1	S	2408–2416	2.9	98.52	0.67	0.05	0.32	0.43	0.72	−30.1	−35.5		−1.4	−149	−224	4.851 ± 0.944	0.03	−5.4
JY1-2	S	2320		98.8	0.7	0.02	0.13	0.34	0.73	−29.9	−35.9		5.9	−147	−199	6.012 ± 0.992	0.04	−6.0
JY6-2	S	2850		98.95	0.63	0.02	0.02	0.39	0.65	−31.1	−35.8		8.9	−149	−191	2.870 ± 1.109	0.02	−4.7
JY7-2	S	2585		98.84	0.67	0.03	0.14	0.32	0.70	−30.3	−35.6		8.2	−143	−158	5.544 ± 1.035	0.04	−5.3
JY8-2	S	2622	3.1	98.75	0.7	0.02	0.21	0.32	0.72	−30.5	−35.6		7.8	−141	−164			−5.1
JY9-2	S	2588		98.56	0.69	0.02	0.2	0.52	0.72	−30.7	−35.4		8.9	−146	−199	5.297 ± 1.086	0.04	−4.7
JY10-2	S	2644		98.66	0.7	0.02	0.26	0.36	0.72	−31.0	−35.9			−148	−186			−4.9
JY11-2	S	2520		98.63	0.69	0.02	0.23	0.42	0.72	−30.4	−35.9		8	−149	−195	5.649 ± 1.225	0.04	−5.5
JY13-3	S	2665		98.57	0.66	0.02	0.25	0.51	0.68	−29.5	−34.7	−37.9		−149	−165			−3.9
JY20-2	S			98.38	0.71	0.02	0	0.89	0.74	−29.7	−35.9	−39.1		−149	−165			−4.4
JY42-1	S			98.54	0.68	0.02	0.38	0.38	0.71	−31.0	−36.1			−147	−166			−5.1
JY42-2	S			98.89	0.69	0.02	0	0.39	0.71	−31.4	−35.8	−39.1		−148	−167			−4.4
JY4-1	S	2800		97.89	0.62	0.02	0	1.07	0.65	−31.6	−36.2			−147	−165			−4.6
Wei201-H3	Є	3647		96.52	0.35		1.24	1.75	0.36	−35.4	−40.8			−145		4.348 ± 0.662	0.03	−2.5
TL-4	Є									−38.4	−29.8							8.6
TL-6	Є									−35.8	−31.1							4.7
TL-7	Є									−38.0	−30.4							7.6
TL-8	Є									−36.5	−30.7							5.8
TL-10	Є									−35.3	−29.9							5.4
TL-11	Є									−35.0	−29.2							5.8
TL-12	Є									−39.6	−32.8							6.8
TL-13	Є									−33.8	−39.6							−5.8
TL-16	Є									−35.3	−28.3							7.0
TL-17	Є									−34.1	−29							5.1
TL-18	Є									−34.7	−30.3							4.4
TL-19	Є									−39.2	−32.7							6.5
TL-20	Є									−36.7	−33.1							3.6

typically implies the existence of mantle-derived helium, whereas an R/Ra < 0.1 often indicates a crustal origin for helium (Schoell, 1983; Xu et al., 1998). Based on these criteria and an R/Ra value of 0.01–0.04 for the Palaeozoic shale gas, a crustal origin for the gases is proposed.

3.2. Isotopes of the Lower Paleozoic shale gas

Isotope geochemistry is a unique tool for shale gas exploration (Tilley and Muchlenbachs, 2013). However, the mechanism for the generation of isotopically reversed gases is controversial. Previous studies have identified numerous mechanisms, including redox reactions (Burruss and Laughrey, 2010), water reforming of residual organic matter (Zumberge et al., 2012), the mixing of biogenic and abiogenic gases, and the mixing of gases from sapropelic and humic sources (Dai et al., 2016). Tilley et al. (2011) emphasized that isotopically reversed gas is a mixture resulting from the conventional maturation of kerogen and the cracking of residual oil, which is usually restricted to sealed, self-contained hydrocarbon systems similar to shale gas systems. Tilley's later research proposed an association of isotopic reversals with the universal stages and trends of gas maturation in sealed, self-contained petroleum systems (Tilley and Muchlenbachs, 2013). Therefore, it can be concluded that isotopically reversed gases are often confined to sealed hydrocarbon systems. Shale gas with isotopic reversals can be found in sealed systems with highly productive shale gas.

In the Lower Silurian shale gas, $\delta^{13}C_1$ ranges from −26.7‰ to −37.3‰, with an average of −31.4‰, while $\delta^{13}C_2$ ranges from −37.9‰ to −42.8‰ in the Sichuan Basin (Table 1). $\delta^{13}C_{methane}$ (C_1) versus $\delta^{13}C_{ethane}$ (C_2) cross plot illustrate Longmaxi shale gases are in carbon reversal zone (Fig. 4). In the Lower Silurian shale gas, $\delta^{13}D_{CH4}$ ranges from −138‰ to −157‰, while $\delta^{13}D_{C2H6}$ ranges from −179.9‰ to −172.8‰, showing hydrogen isotopic reversals both in the Weiyuan gas field and in the Fuling gas field (Table 1). The Lower Silurian shale gas is highly productive as we mentioned before. We therefore conclude that our data support Tilley's theory that high productivity is closely related to isotopic reversals in shale gas. Shale gas production have positive correlation with the absolute value of ($\delta^{13}C_2$- $\delta^{13}C_1$) (Fig. 5). It means more isotopic reversals indicates higher gas production. Furthermore, isotopic reversals can be used to estimate the sealed volume.

However, there exist isotopically normal gases in the Cambrian rocks, with $\delta^{13}C_1$ ranging from −39.6‰ to −33.8‰, with an average of −36.3‰; and $\delta^{13}C_2$ ranging from −39.6‰ to −28.3‰, with an average of −31.3‰.It shows normal isotopic trend ($\delta^{13}C_1 < \delta^{13}C_2$). This may indicate that the Cambrian petroleum system was a continued open system when oil and gas generated and migrated. Shale gas isotopic reversals are commonly encountered due to mixing processes or some reactions in sealed system, especially the mixing of primary and secondary products in source rock of varying maturity (Dai et al., 2004; Xia et al., 2013; Tilley and Muchlenbachs, 2013). Under the relatively open system, fluids generated from source rock can migrate out smoothly, and hydrocarbon from different stages are separated significantly. Gases generate in early stage are difficult to accumulate and remain in-situ and mixed gases are absent. So it always displays the normal isotopic distribution trend in open petroleum system, like most conventional petroleum reservoirs and permeable fractured reservoirs. We

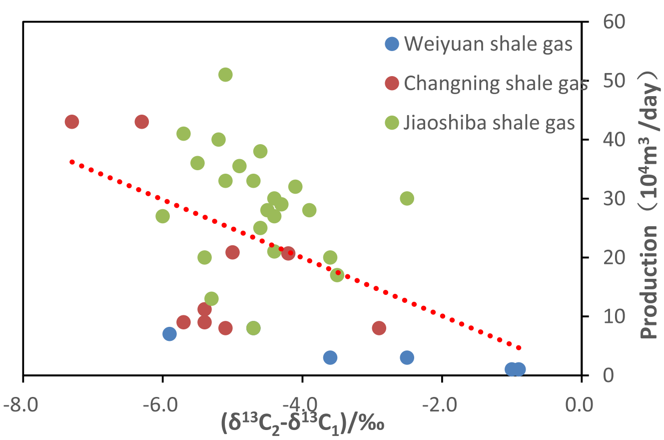

Fig. 5. Relationship of shale gas production with value of ($\delta^{13}C_2$- $\delta^{13}C_1$).

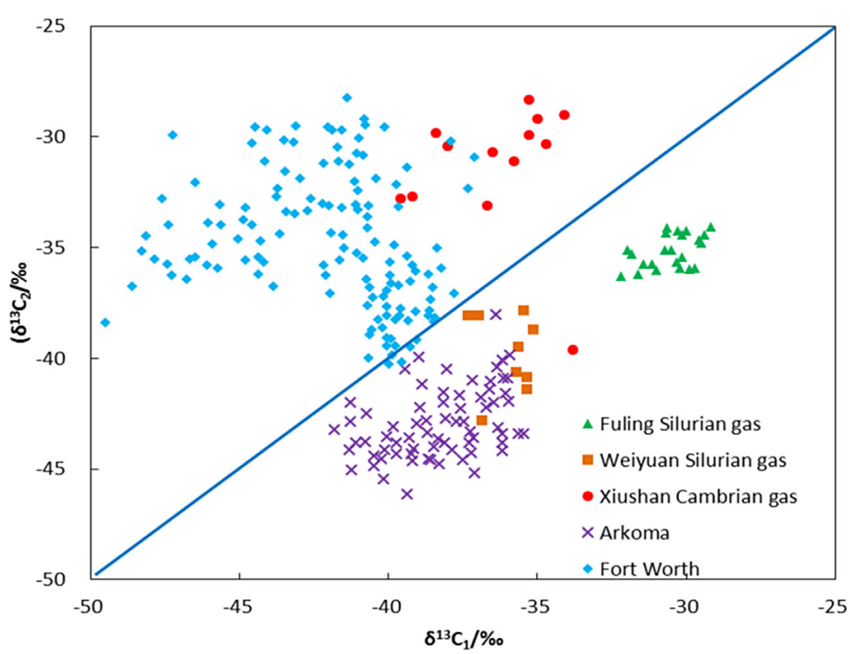

Fig. 4. Relationship of $\delta^{13}C_2$ to $\delta^{13}C_1$ in shale gas systems in China and North America.

conclude the Lower Cambrian black shale may be under a relatively open system conditions in the evolution history of gas generation and migration, supported by the normal isotopic trend, as well as gas content and production that are much lower than those of the Lower Silurian black shale. Other evidence such as pressure coefficients support this interpretation, as discussed later.

4. Pressure coefficients

The pressure coefficient is an important index in evaluating the initial reservoir pressure. The pressure coefficient value is defined by the ratio of the bottom hole pressure to the equal reservoir depth hydrostatic pressure. The pressure coefficient (*Cp*) is estimated using the equation:

$$Cp = \frac{Pt}{Ph} \quad (1)$$

$$Ph = \rho \text{gh} \quad (2)$$

where *Pt* is the test ratio of the test bottom hole pressure, *Ph* is hydraulic pressure, ρ is the density of the liquid (water), h is the depth of the reservoir, and g is 9.8 m/s^2. A $Cp > 1.0$ represents abnormally high pore-fluid pressure or formation pressure (overpressure). A $Cp < 1.0$ represents abnormally low pressure.

Hydrocarbon expulsion begins at the moment the source rock generates hydrocarbon. For type I and II kerogen, shale rich in organic matter first generates oil when it is within the "oil window". As the thermal evolution continues to a high enough maturity, the oil cracks into gas and the bitumen remains. The generation of natural gas has been proven to be a significant factor for overpressurization (Barker, 1990; Osborne and Swarbrick, 1997; Swarbrick et al., 2002; Tingay et al., 2013). Pressure (or the pressure coefficient) can be used to evaluate the reservoir preservation In a confined volume (as with shale), gas generation will result in a pressure increase as thermal evolution progresses. Overpressurization conditions and high *Cp* are generally considered to be generated by fluid expansion (kerogen to oil or gas, oil cracks to gas) in sealed, self-contained shale gas system. Therefore, pressure and Cp can indirectly reflect the extent that fluids have migrated from the shale. The less that fluids have migrated, the higher that reservoir pressures will be. Besides, the discussion of oil thermal cracking and fluids expansion here is under the hypothesis of equal adsorption of source rock. Gas adsorption is innegligible in rich organic matters shale, and we anticipate continued research in this area for some time to come.

A strong correlation exists between production and *Cp*. Higher *Cp* always results in higher production. Complicated hydrocarbon thermal cracking and fluid migration over the long-term evolution can be ignored because present pore-fluid pressures can indicate the remaining volume of hydrocarbon. This shows that the Longmaxi shale is overpressurized in the Sichuan Basin, with *Cp* between 1.45 and 2.03 (Table 2). Overpressurization could indicate that abundant gas remains. Many wells are highly productive. However, the Qiongshuzi shale has a normal pressure, with a *Cp* of approximately 1.12 (Table 2). This shows that most of the gas has been transferred from the shale into other formations.

Two wells from the Weiyuan shale gas field were analysed to identify the relationship between production and pressure. Well Wei204 and well Wei201 are from the same gas field and have the same geologic settings, but experience a large difference in production. In well Wei 204, the Longmaxi shale gas production is 16.51 m^3/d and the *Cp* is 2.2. However, in well Wei201, the Qiongshuzi shale gas production is only 1.08 m^3/d, while *Cp* is 1.12. The *Cp* of Wei204 is twice that of Wei201, but the gas production of Wei204 is 15 times higher than that of Wei201. The data show that the Qiongzhusi Formation pressures are lower than that of the Longmaxi Formation, as is the production. This also indicates that the Qiongshuzi shale transferred so much hydrocarbon material that it retains little gas in this area.

5. Solid bitumens

Solid bitumens have been found worldwide in numerous petroliferous basins with diverse forms, and their origins, as well as their biochemical markers, can be used to detect hydrocarbon migration and accumulation (Curiale, 1986; Xu et al., 2007). Curiale genetically classified the solid bitumens as either pre-oil and/or post-oil based on H/C atomic ratios, moretane/hopane ratios, and ratios of sterane isomers (Curiale, 1986). This genetic classification is used to trace the origin of solid bitumens. Numerous studies have investigated the Sinian Dengying Formation reservoir solid bitumens (Xu et al., 1998, Xu et al., 2007; Huang et al., 2015). In this study, we use previous biomarker data to analyse the origin of the solid bitumens (Xu et al., 2007; Huang et al., 2015). The distribution and quantity of the solid bitumens are also used to determine hydrocarbon expulsion and migration.

5.1. Origins of solid bitumens

5.1.1. Biological markers

Biological marker analysis of solid bitumens and their extracts can be used to trace the origins of solid bitumens (Curiale, 1986; Xu et al., 2007). In this study, we compiled the majority of previously published geochemical data associated with the origin of the solid bitumens from this area, and reorganized and interpreted these data. The observation of cores and outcrops shows that the Sinian Dengying Formation is a dolomite reservoir with extensive occurrence of solid bitumens. The solid bitumens were mainly found in the dissolved fractures, vugs and intercrystalline pores in the

Table 2
Production and pressure coefficients of shale gas wells in the Sichuan Basin.

Areas	Wells	Formation	Depth (m)	Production (10^4 m^3/d)	Pressure coefficient
Weiyuan	Wei201-H1	Longmaxi	2823	1.31	0.92
Gas field	Wei204	Longmaxi	3550	16.51	1.96
	Wei203-H3	Qiongzhusi	2135	1.80	1.12
	Wei201	Qiongzhusi	2823	1.08	1.12
Fushun	Yang201-H2	Longmaxi	3577	43.00	2.20
Gas field	YS108H1-1	Longmaxi	3564	20.86	2.00
Changning Gas field	Ning201-H1	Longmaxi	3790	14.50	2.03
	NingH3-1	Longmaxi	4448	7.68	2.00
Jiaoshiba Gas field	Jiaoye1	Longmaxi	2420	20.30	1.45
Pengshui Gas field	Pengye1	Longmaxi	2396	2.30	1.00

Table 3
Biomarkers of the Sinian Dengying Formation bitumens and Cambrian shale samples.

Number	Samples	Formation	Depth (m)	Carbon numbers of n-alkanes	Odd/even predominance (OEP)	Carbon Preference Index (CPI)	Ts/Tm	Tricyclic terpane/C_{30} hopane
1	Black shale	$Є_1q$	4972.7	18	1.12	1.15	0.87	0.36
2	Black shale	$Є_1q$	4974.9	25	1.1	1.19	0.86	0.34
3	Black shale	$Є_1q$	3478.76	25	1.13	1.19	0.64	0.4
4	Black shale	$Є_1q$	3479.97	24	1.09	1.2	0.76	0.63
5	Black shale	$Є_1q$	outcrop	18	1.01	1.16	0.62	0.58
6	Black shale	$Є_1q$	outcrop	18	1.03	1.12	0.6	0.53
7	Black shale	$Є_1q$	4987.25	20	1.1	1.13	0.82	0.57
8	Bitumens in vugs	Z_2dn	5149.08	19	1.23	1.21	0.76	0.28
9	Bitumens in dissolved pores	Z_2dn	5152.66	19	1.11	1.19	0.86	0.55
10	Bitumens in fractures	Z_2dn	5441.1	18	1.1	1.21	0.86	0.67
11	Bitumens in vugs	Z_2dn	3490.26	19	1.07	1.13	0.67	0.53
12	Bitumens in vugs	Z_2dn	3494.67	23	1.06	1.16	0.67	0.84
13	Bitumens in vugs	Z_2dn	3499.7	23	1.06	1.15	0.58	0.74
14	Bitumens in vugs	Z_2dn	3500.05	23	1.05	1.17	0.62	0.74
15	Bitumens in intercrystalline pores	Z_2dn	3513.47	22	1.01	1.1	0.6	0.78
16	Bitumens in intercrystalline pores	Z_2dn	3654.36	23	1.03	1.13	0.64	0.81
17	Bitumens in vugs	Z_2dn	outcrop	25	1.05	1.16	0.67	0.82
18	Bitumens in intercrystalline pores	Z_2dn	outcrop	27	1.07	1.1	0.67	0.76
19	Bitumens in intercrystalline pores	Z_2dn	outcrop	25	1.13	1.14	0.58	0.55
20	Bitumens in intercrystalline pores	Z_2dn	outcrop	24	1.01	1.12	0.62	0.67
21	Bitumens in vugs	Z_2dn	outcrop	20	1.04	1.16	0.64	0.53
22	Bitumens in vugs	Z_2dn	outcrop	18	1.05	1.17	0.78	0.84
23	Bitumens in intercrystalline pores	Z_2dn	outcrop	23	1.11	1.15	0.74	0.82

dolomite. Solid bitumens samples from the Sinian Dengying dolomite reservoir and from the Cambrian Qiongzhusi Formation source rocks (shale and mudstone) were collected for gas chromatography–mass spectrometry (GC–MS) analysis (Table 3).

Multiple factors can influence the biomarkers of bitumens. If the solid bitumens originate in the source rock, their biomarkers should show the same or similar characteristics. Table 3 shows that the carbon numbers of n-alkanes of the Cambrian Qiongzhusi Formation source rocks range from 17 to 25. The solid bitumens from the Sinian Dengying exhibit a similar n-alkane distribution, with carbon numbers ranging from 18 to 27. The n-alkane distribution yielded a close correlation.

The OEP (odd/even predominance) and CPI (carbon preference index) are very similar for both the solid bitumens and shale samples. The Pr/Ph of both bitumens and shale are similar, ranging from 0.38 to 0.67. Therefore, the theory of Peters and Moldowan (1993) indicates that phytane dominates in these samples. The low Pr/Ph also indicates that the source rocks originate in anoxic depositional environments.

Liang and Chen proposed that some biomarkers are invalid when the maturity is too high (Liang and Chen, 2005). The maturity of the bitumens in this study ranges from 3.46% to 4.51%, and maturity of most shale samples are over 2.4%. Both the bitumens and shale exhibit high maturity. The Ts/Tm ratio is dependent on maturity and the depositional environment (Peters et al., 2005). Xu used Ts/Tm as well as the tricyclic terpane/C_{30} hopane ratio to distinguish between the origins of source rocks and bitumens when the maturity is very high (Xu et al., 2007). The results show that the biomarkers of the Sinian reservoir solid bitumens are similar to those of the Cambrian shale samples. Additionally, previous studies used diasteranes/regular steranes, gammacerane, pregnane and other biomarkers to determine that the solid bitumens from the Sinian Dengying Formation and from the Cambrian Qiongzhusi Formation shale are syngenetic.

5.1.2. Carbon isotopic values

Isotopic measurements of individual hydrocarbons can be used to determine their origins, as the hydrocarbon products that are generated from organic-rich source rocks should have similar to or lower carbon isotopic value than the source rocks (Marais et al., 1981). The carbon isotopic values of solid bitumens from the Sinian Dengying Formation range from −37.0‰ to −34.5‰, which differ from the Sinian source rock carbon isotopic values that range from −33.0‰ to −28.5‰. The carbon isotopic values of the Cambrian shale range from −36.5‰ to −31.5‰, which is more similar to the carbon isotopic values of solid bitumens from the Sinian Dengying Formation. This further supports that the solid bitumens in the Sinian Dengying Formation reservoir originate in the Cambrian Qiongzhusi Formation.

5.2. Bitumen distribution

The presence of hydrocarbon expulsion channels results in poor hydrocarbon source rock preservation and small volumes of remaining hydrocarbon, while the surrounding layers increase in hydrocarbon volume. Large volumes of hydrocarbon are also present in the migration pathway. Bitumens provides direct evidence for hydrocarbon reservoirs, and also suggests hydrocarbon migration during the evolution process. Extensive research on the Sinian Dengying Formation hydrocarbon accumulation, gas generation conditions process of the hydrocarbon source rock were performed, especially the bitumen distribution in the Dengying Formation and the close relation with Lower Cambrian (Huang et al., 2011; Liu et al., 2016). The bitumens distribution in the Dengying Formation is widespread and originates in the Lower Cambrian Qiongzhusi Formation.

Using the Weiyuan gas field as an example, the Sinian Dengying Formation bitumens content varies widely between approximately 65.66% and 90.02% according to core slice observation. Bitumens are mainly found 100 m below the Tongwan unconformity surface (Fig. 7). Therefore, the widespread bitumens distribution in the Sinian Dengying Formation may be a result of favourable hydrocarbon migration channels formed by the Tongwan unconformity surface. Unconformity surfaces provide continued open system, as well as the major oil migration channels in early stages and gas dispersion channels after crude oil pyrolysis when the maturity of source rock is proper. Unconformity surfaces permitted significant hydrocarbon migration and dispersion, resulting in poor gas content in the source rocks. The Baota Formation neighbours the Longmaxi Formation; however, no widely distributed bitumens or other hydrocarbons have been observed in those rocks. This indicates that significant volumes of hydrocarbons did not experience migration and dispersion from the Longmaxi Formation during the evolution process.

6. Differential fluid migration behaviour in Lower Silurian and Lower Cambrian shale gas systems

6.1. Total organic carbon (TOC) content and gas content

Gas geochemical data, pressure coefficients and the distribution of solid bitumens in the adjacent reservoir show that the Lower Silurian and Lower Cambrian shales have different fluid migration histories. Gas content is a direct indicator for the quality of a shale gas reservoir. Gas content has positive correlation with total organic carbon (TOC) content in many productive shale gas fields (Ross and Bustin, 2007). In this study, data from two wells from the same area were analysed to determine the differences in gas content (Fig. 6). Fig. 6 shows that the TOC of the Well Yucan 4 in the Lower Silurian Longmaxi shale is 1–2% and that the Lower Cambrian shale has a higher TOC of 2–8%. However, gas content of the Longmaxi is 1.6–2.5 m^3/t, while that of the Qiongzhusi shale is only 0.1–0.3 m^3/t. The high TOC of the Qiongzhusi shale indicates that it has a good source rock and has generated abundant hydrocarbons during its history. The low gas content today is the result of strong hydrocarbon expulsion (see Fig. 8).

6.2. Cause of differential fluid migration behaviour

Shale gas accumulation is mainly controlled by tectonic movement and preservation conditions (Nie et al., 2012; Guo, 2016; Liu et al., 2016). Shale gas reservoirs differ from conventional gas reservoirs in that shale and black mudstone are simultaneously both the reservoir and the source rock. Gas content is mainly controlled by the volume of hydrocarbon generated from the source rock and by the remaining volume of gas after complicated thermal cracking and migration out of the reservoir. A shale rich in organic matter can continuously expel hydrocarbon until thermal evolution ends. The present shale gas, which contains both absorbed gas and free gas, is the remaining hydrocarbon in the source rock. The present remaining shale gas content is mainly controlled by hydrocarbon migration when the source rocks have the same or similar gas generation. If the same hydrocarbon volume is generated, fewer hydrocarbons migrate out of or are expelled from the shale, and more shale gas remains today. The migration and expulsion we refer to here are associated with the primary migration, namely, a complex process based on the interplay of chemical reactions creating fluids, mass transfer in low permeability rocks and finally source rock compaction (Rudkiewicz et al., 1994“).

In the process of hydrocarbon migration from the source rock, the more permeable channels such as faults and unconformities may dominate. A permeable unconformity near the source rock can result in large volumes of hydrocarbons migrating from the source rock over time, leaving little shale gas remaining today. The stratigraphic sequences of the Sichuan Basin (Fig. 1), indicate that a distinct unconformity formed at the bottom of the Cambrian Qiongzhusi source rock during the Tongwan period. We hypothesize that the Tongwan unconformity was the main cause of extensive hydrocarbon migration, as it connects a good conventional reservoir with more than 400×10^8 m^3 of hydrocarbons in the Dengying Formation below the Tongwan unconformity. The reservoir bitumens we discussed previously support this hypothesis. However, with the existence of the Tongwan unconformity, abundant hydrocarbons were able to migrate into the other formations, leaving little remaining gas in the Qiongzhusi shale. This is a relatively open system where it is difficult to maintain a high *Cp* within the shale. It is therefore difficult to form a good shale gas reservoir in the Qiongzhusi shale.

In contrast, there are no permeable channels, such as large unconformities or faults, near the Longmaxi Formation. There is also a thick and stable gypsum layer above the Longmaxi source rock and a compact limestone layer with low permeability under the Longmaxi source rock. This shale formation can therefore retain

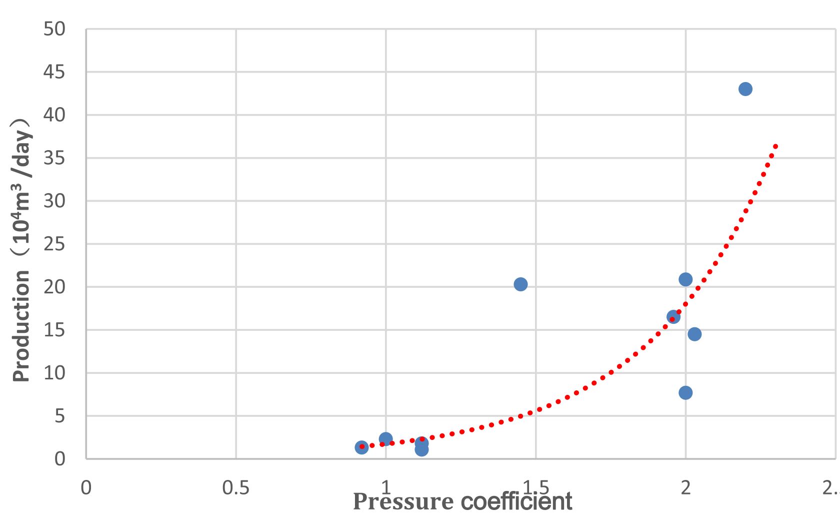

Fig. 6. Relationship between shale gas production and pressure coefficients in shale gas wells.

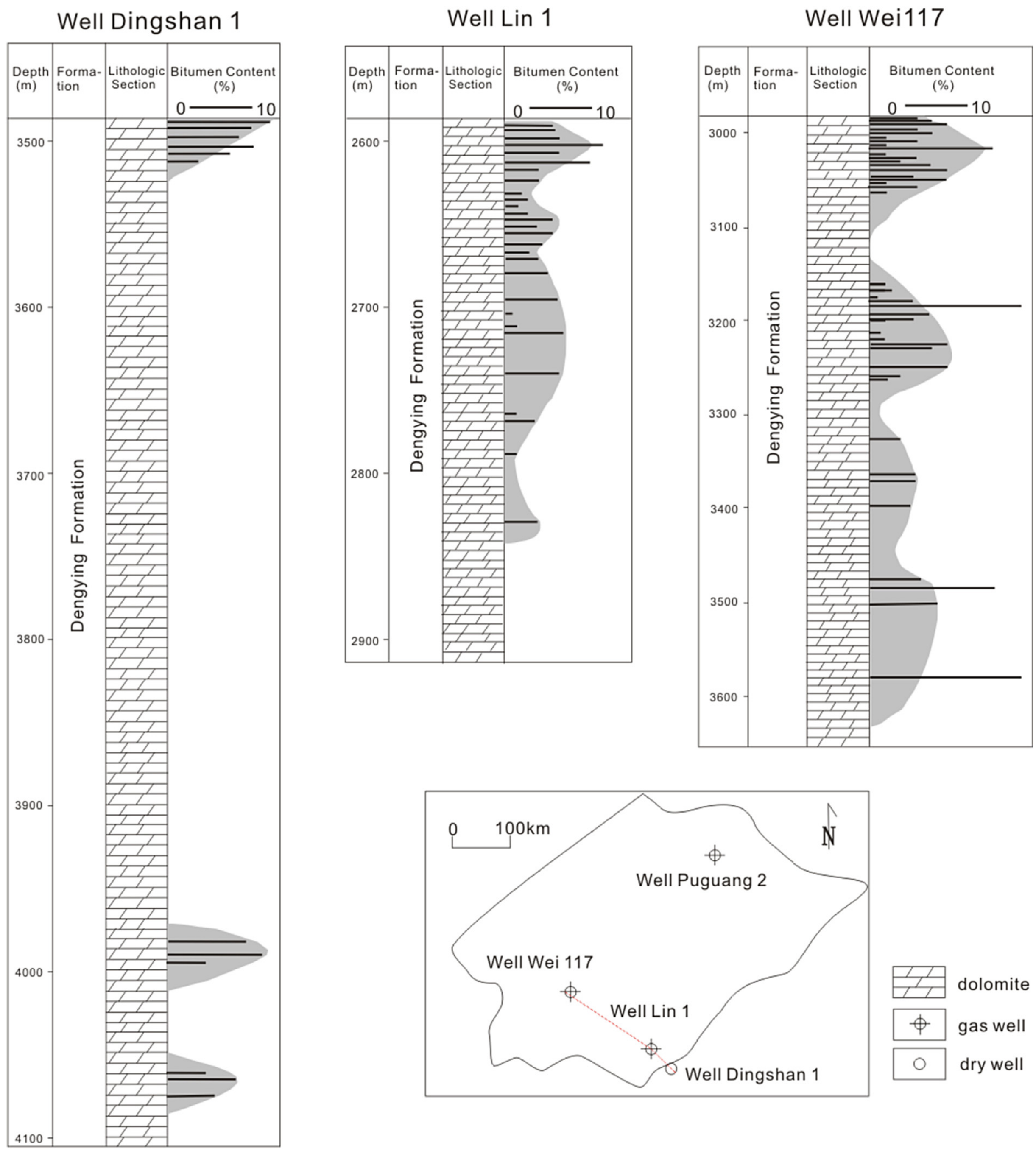

Fig. 7. Bitumens distribution in the Sinian Dengying Formation.

hydrocarbon very well and can preserve high pressures after oil or gas thermal cracking. Numerous shale gases have been found in the Longmaxi shale formation, which contributed 90% of the shale gas production in China over the last decade. Note that the diffusion of gas always occurs in the source rock. The source rock can continuously generate hydrocarbon and can permit migration of the oil and gas out of the source rock under the proper circumstances, even if there are no very highly permeable channels. We emphasize that a large volume of gas migrated out of the source rock as a result of the Tongwan unconformity and that this is main reason for the failed shale gas exploration in the Qiongzhusi Formation. Significant volumes of gas also migrated out of the Longmaxi shale, but abundant gas remains within the shale, allowing it to be a productive shale gas today.

7. Conclusions

This paper provide a method to assess the preservation conditions and explain the differential fluid migration behaviour in shale gas reservoir, through the isotope geochemistry, pressure coefficients and bitumens distribution analyses. Observations in isotopically normal gases, low pressure coefficients and widespread distribution of bitumens proved an open petroleum system and fluid migration path of Lower Cambrian Shale caused by Tongwan tectonic unconformity, which resulted in poor gas content and low productivity.

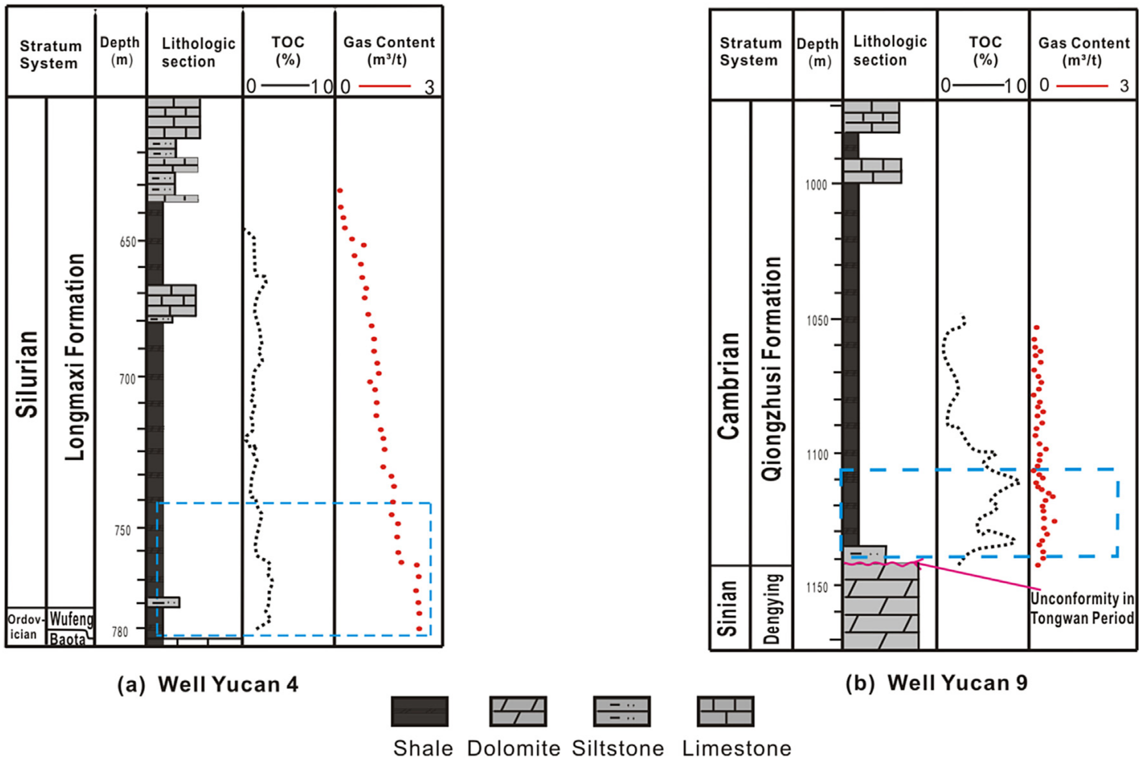

Fig. 8. TOC content and shale gas content of Wufeng-Longmaxi Formation(a) and Qiongzhusi Formation(b) in Sichuan Basin and surrounding areas.

(1) Carbon isotopic reversal ($\delta^{13}C_1 > \delta^{13}C_2$) and hydrogen isotopic reversal ($\delta^{13}D_{C2H6} > \delta^{13}D_{CH4}$) are observed in the Lower Silurian shale gas. Isotopically reversed gases suggest that the Lower Silurian shale gas is a sealed, self-contained petroleum system. Besides, isotope "reversals order" degree of shale gas has positive correlation with gas production. While, isotopically normal gases from the Lower Cambrian suggest that it is an open petroleum system. We propose that the Tongwan tectonic movement opened the petroleum system and induced the poor gas preservation in Qiongzhusi shale.

(2) We conclude that the Lower Silurian shale gas reservoir is an overpressurized system, with pressure coefficients ranging from 1.45 to 2.03. Overpressurization also indicates that the gas is within a sealed and self-contained system. Good relationships have been found between shale gas production and pressure coefficients. However, there is a normal pressure system in the Lower Cambrian shale gas reservoir, which indicates that it is continued open system, which resulted in poor gas content and low productivity.

(3) Result of individual hydrocarbon isotope and biomarker analysis shows solid bitumens in Sinian Dengying Formation originate from Lower Cambrian source rock. The bitumens were mainly found 100 m below the Tongwan unconformity surface and widespread in the Sinian Dengying Formation observed by core slice. The Tongwan unconformity provided good "hydrocarbon migration tunnels" between the Sinian dolomite and Lower Cambrian source rocks and is the main cause of differential shale gas content and production performance.

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