

Characteristics and geochemical implications of light hydrocarbons from ultra-deep Ordovician oils in the North Shuntuoguole area, Tarim Basin

Li DONG¹, Anlai MA (✉)¹, Huixi LIN¹, Lu YUN², Weilong PENG¹, Xiuxiang ZHU²

¹ Petroleum Exploration and Production Research Institute, Sinopec, Beijing 102206, China

² Northwest Oilfield Company, Sinopec, Urumqi 830011, China

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Abstract The ultra-deep Ordovician reservoirs in North Shuntuoguole Oilfield (or Shunbei Oilfield) of Sinopec have achieved annual production of one million ton, and the oil & gas in different faults show different physical properties and fluid phases. In this study, the 28 oil samples from the ultra-deep Ordovician were analyzed using whole oil chromatography. The heptane and isoheptane values of the oil samples were in the range of 29.79%–46.86% and 1.01%–3.06%, respectively, indicating the oils are high mature. The maturity that calculated based on light hydrocarbon values was higher than which calculated by using aromatic hydrocarbon parameters, suggesting the light hydrocarbon maturity mostly reflects the maturity of the late charged hydrocarbon. The 2M-/3M-C₅ and 2M-/3M-C₆ ratios varied in the ranges of 1.41–1.81 and 0.79–1.09, respectively, and the *i*C₅/*n*C₅ and 3M-C₅/*n*C₆ ratios were 0.31–0.90 and 0.16–0.37, respectively, indicating that ultra-deep Ordovician reservoirs have not experienced biodegradation. The Mango parameter *K*₁ of the oil samples ranges 0.96–1.01 except for the oil from Well SB4, which suggests that most of the reservoirs have not suffered thermochemical sulfur reduction (TSR). Meanwhile, the oils have not experienced evaporative fractionation since the toluene/*n*C₇ and *n*C₇/MCC₆ ratios range from 0.10–0.38 and 1.50–1.80, respectively. The close correlation between P₃ and P₂ + N₂ and between P₂ and N₂/P₃ indicates that the oils from different faults have the same origin. According to the characteristics of LHs rich in *n*-alkane, as well as other biomarkers, such as aryl isoprenoids, and aromatic hydrocarbon parameters, the oil originated from the source rock of Lower Cambrian Yu'ertusi Formation. Meanwhile, the source rocks in different fault zones slightly differed in organic facies.

Keywords light hydrocarbons, biodegradation, thermochemical sulfate reduction (TSR), evaporative fractionation, ultra-deep Ordovician reservoir, Tarim Basin

1 Introduction

Light hydrocarbons (LHs) account for greater than 30% of crude oil and over 90% of light oil and condensate oil (Hunt, 1984). Therefore, the geochemical information obtained from LHs is more important and representative for light oil, volatile oil and condensates (Song et al., 2016). LHs are widely applied in the determination of petroleum maturity (Thompson, 1979, 1983; Cheng et al., 1987; Wang et al., 2010), the classification of oil genetic types (Mango, 1987, 1997; Lin and Zhang, 1998; Zhang et al., 1999; Zhu and Zhang, 1999), determination of oil family and source rocks (Hu et al., 1990; Mango, 1997), characterization of the sedimentary environment and organic input (Hu et al., 1990) and identification of secondary alteration, such as biodegradation (Harris et al., 2003; Yang et al., 2015), thermochemical sulfate reduction (TSR) (Mango, 1997; Song et al., 2016, 2017) and evaporative fractionation (Thompson, 1987, 1988, 2010; Zhang et al., 2011; Sun et al., 2013; Xiao et al., 2011).

Sinopec discovered North Shuntuoguole Oilfield (also named Shunbei Oilfield) in Shuntuoguole area, dominated by fault-karst reservoirs and light oil and volatile oil phases (Jiao, 2018). But there are different opinions on the pool-forming period and secondary alteration of Ordovician reservoirs in North Shuntuoguole area. Qi (2020) suggested that the pools in North Shuntuoguole area were mainly formed in Yanshanian-Himalayan Period. Yang et al. (2020) argued that the pool in the ultra-deep Ordovician strata in Well Manshen 1 on the north part of fault No. 4 (F4) was formed in the late Hercynian Period. Ma et al. (2020) suggested that the key

to preservation of light oil and volatile oil reservoir phases in the Ordovician in the area is the weak secondary alteration of the oil reservoirs, along with the long term low-geothermal background. [Chai et al. \(2020\)](#) proposed that the reservoirs in No.1 Fault (F1) have undergone evaporative fractionation to a certain extent, while that in the northern of No.5 Fault (F5) experienced little. [Cheng et al. \(2020\)](#) concluded that reservoirs in the Shuntuoguole area have not experienced evaporative fractionation.

Available literature focuses on geochemical research of oil reservoirs in F1 and F5 North ([Cao et al., 2020](#); [Chai et al., 2020](#); [Cheng et al., 2020](#); [Ma et al., 2020](#); [Wang et al., 2021](#)). However, with the continuous progress in oil and gas exploration in the area, new breakthroughs have been made in F5 Middle, F5 South and F4. In this study, 28 oil samples were taken from different faults in the ultra-deep Ordovician in the North Shuntuoguole area and were analyzed by whole oil chromatography. The paper focused on the application of LHs in maturity evaluation for ultra-deep oils and secondary alterations (such as biodegradation, TSR and evaporative fractionation) of the ultra-deep reservoirs. The results would contribute to a better understanding the ultra-deep oil & gas accumulation mechanism in the Tarim Basin.

2 Geological background

North Shuntuoguole area is located in the northwest of the Shuntuoguole Low Uplift in the Tarim Basin and at southwestern pitching end of the Shaya Uplift. It spans the eastern slope of Awati Depression in west and adjoins Manjiaer Depression in the east. Shuntuoguole Low Uplift, with a gentle structure, is high in north and east, and low in south and west ([Fig. 1](#)) ([Jiao, 2018](#); [Qi, 2020](#)). Ordovician strata are well developed in the Shuntuoguole area, including the Lower Ordovician Penglaiba Formation (O_{1p}), Middle-Lower Ordovician Yingshan Formation (O_{1+2y}), Middle Ordovician Yijianfang Formation (O_{2y}), and the Qiaerbake (O_{3q}), Lianglitage (O_{3l}), and Sangtamu Formations (O_{3s}) of the Upper Ordovician from bottom to top. Among them, the carbonate rocks of the Ordovician Yijianfang–Yingshan Formations and the overlying thick mudstone cap rock of the Sangtamu Formation form favorable reservoir-cap rock assemblages, which are the main targets of oil and gas exploration and assessment. The reservoir types include cavities and tectonic fractures related to strike-slip faults and corroded holes and cavities along the fractures ([Jiao, 2018](#); [Qi, 2020](#)).

The oils in the Ordovician in the area mainly include light oil and volatile oil, while the oils discovered in

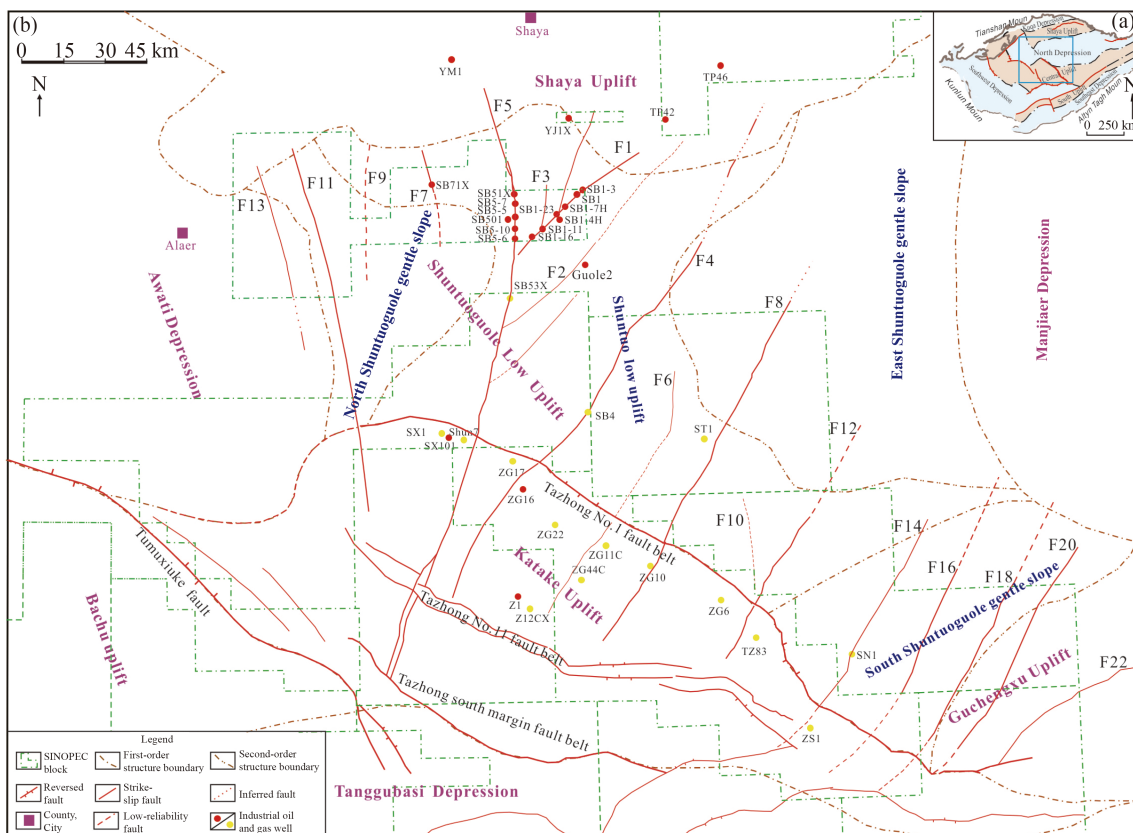


Fig. 1 Location of North Shuntuoguole area and distribution of wells, Tarim Basin.

southern wells SB53X and SB4 are condensate. Controlled by strike-slip fault zones, the reservoirs are distributed along the strike-slip fault zones horizontally and mainly spread in the planes and fractured zones of the faults vertically. At present, the exploration and assessment of the Ordovician in the area are mainly targeted at the 18 strike-slip fault zones cutting through the basement and connecting source rocks (Qi, 2020). Among them, F1, F5, and F7 are at a high rolling development stage, with an annual production of one million tons of light oil by the end of 2020. In 2020, the Tarim Oilfield Company of PetroChina discovered oil and gas in Well Manshen 1 located in the north part of F4, achieving a daily production of 624 m³ of oil equivalent and 37.13 × 10⁴ m³ of natural gas equivalent (Yang et al., 2020).

3 Samples and experiment

3.1 Samples

Oil samples were taken from exploration and development wells drilled in F1, F5, F7 and F4 in the area. The oil samples from F1 and F5 Middle are volatile oil, while the samples from F7 and Well SB4 in F4 are light oil and condensate oil, respectively.

3.2 Whole oil chromatography

Whole oil chromatography analysis was conducted by an HP Agilent 6890N gas chromatograph fitted with an HP-PONA quartz capillary column (50 m × 0.20 mm × 0.30 μm). The GC oven temperature was initially set at 35°C with a hold time of 10 min and programmed to 300°C at a rate of 4°C/min with a final hold time of 50 min. N₂ was used as the carrier gas with a constant flow of 1.0 mL/min. The temperatures of injector and flame ionization detector (FID) were set at 300°C and 300°C, respectively. Split mode was used with split ratio of 50:1.

4 Results and discussion

4.1 Characteristics of whole oil chromatogram

The oil samples from the ultra-deep Ordovician in North Shuntuoguole area preserved abundant LHs except for the oil from Well SB4 in F4, which lost LHs to a certain extent (Fig. 2). The chromatograms, which showed the main peaks of *n*-alkanes with low carbon number, indicated high maturity. All samples had high content of methylcyclohexane (MCH) and low content of aromatic hydrocarbon except for the oil from Well SB4, which had relatively high content of toluene and benzene.

The Pr/Ph ratio of the oil samples ranged from 0.93 to

1.76, suggesting that source rocks were deposited in a slightly reductive sedimentary environment. The sedimentary environment and organic matter types of source rocks can be classified according to Pr/*n*C₁₇ and Ph/*n*C₁₈ ratios (Peters et al., 2005). The oil samples had relatively low Pr/*n*C₁₇ and Ph/*n*C₁₈ ratios of 0.14–0.38 and 0.12–0.47, respectively (Fig. 3). According to cluster analysis, the oil samples from F1 and F5 Middle, with Pr/*n*C₁₇ and Pr/*n*C₁₈ ratios in the ranges of 0.33–0.38 and 0.42–0.46, respectively, belonged to the same category (Fig. 3), indicating that the source rocks of the type II organic matters of marine algae. In contrast, the samples from wells SB71X and SB4 showed relatively low Pr/*n*C₁₇ and Ph/*n*C₁₈ ratios, reflecting the source rock consisting of mixed type II/III organic matters.

4.2 Oil maturity

Thompson (1983) proposed that the oil maturity can be identified according to the heptane and isoheptane values of LHs, and the distribution of these values is also controlled by the types of source rocks. Thompson (1983) provided the evolution curves of two types of organic matters, aliphatic and aromatic curves, in the heptane and isoheptane values of which mature oil ranged 22%–30% and 1.2%–2.0%, and those of high-maturity oil are 30%–60% and 2.0%–4.0%, respectively. Cheng et al. (1987) divided the terrigenous oils and condensate oils in China into four categories according to their heptane and isoheptane values, low-maturity oil (including early condensate oil and biodegraded heavy oil), mature oil, high-maturity oil and over-maturity oil, respectively. In this study, the heptane and isoheptane values of the oil samples from different faults in North Shuntuoguole area were 29.79%–46.86% and 1.01%–3.06%, respectively (Fig. 4, Table 1). According to the aforementioned classification standard, the oils in the Ordovician in North Shuntuoguole area are high-maturity oil. Chai et al. (2020) suggested that the heptane and isoheptane values of the oil samples from F1 and the F5 North are 31.7%–38.6% and 1.55%–2.48%, respectively, with an average of 36.2% and 2.12%, respectively. In this study, in terms of the isoheptane values, the samples from Well SB71X in F7 and Well SB4 in F4 showed the lowest and highest values, which were 1.01 and 2.91–3.06, respectively. Meanwhile, the samples from F4 also showed high heptane values, indicating the oil from Well SB4 has highest maturity. According to the classification standard proposed by Walters et al. (2003), the oil in the Ordovician in the area has a maturity *R*_c of 1.1%–1.5%.

The maturity can be identified using the *n*C₇/MCH ratio. The high-maturity oil and condensate oil generated in the late oil generation stage have generally experienced notable oil cracking, with *n*C₇/MCH ratio greater than 1.5, reflecting the equivalent vitrinite reflectance *R*_o >1.2% (Thompson, 1987). In this study, the *n*C₇/MCH ratio of

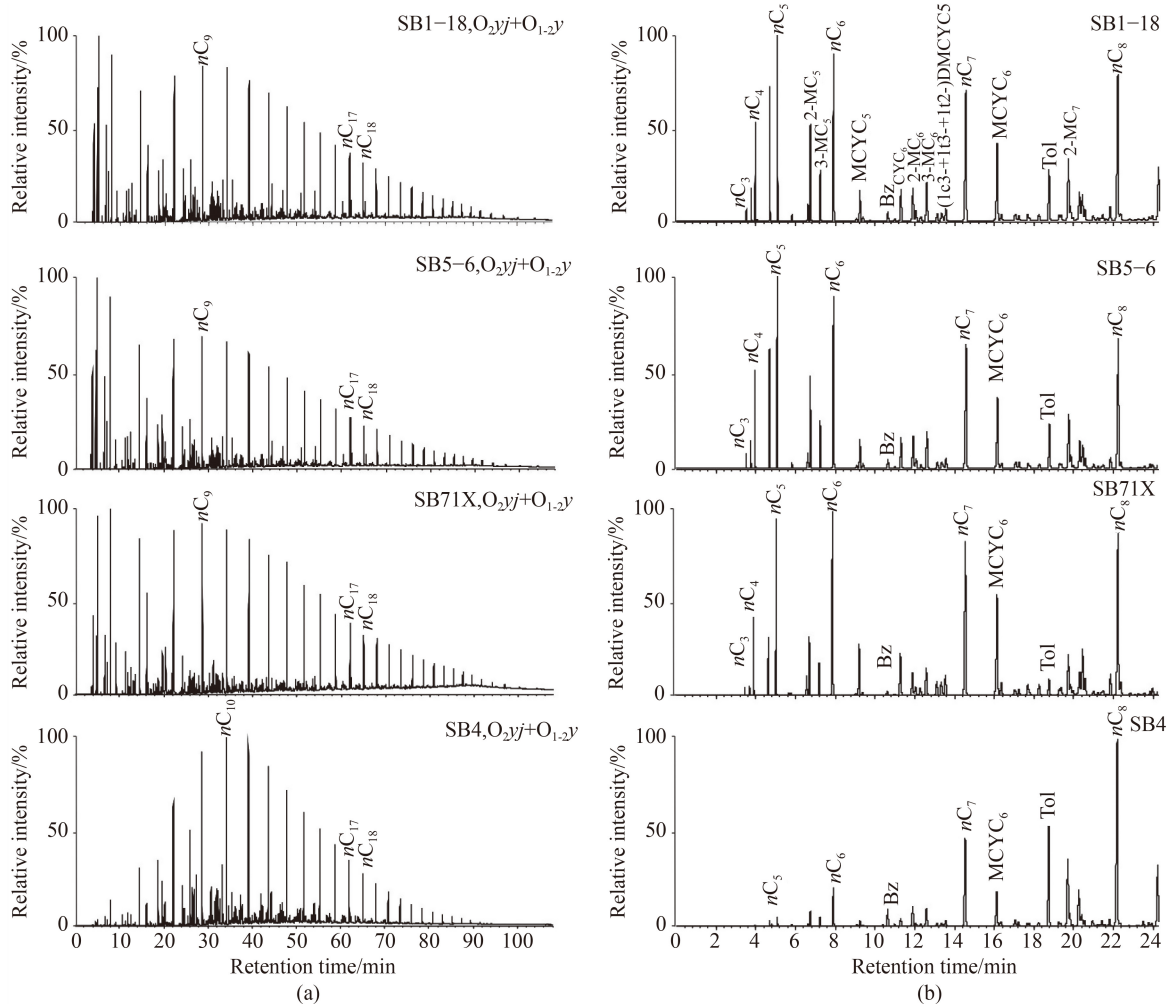


Fig. 2 (a) Whole oil gas chromatograms and (b) C_2 – C_8 light hydrocarbons gas chromatograms of oil samples from the ultra-deep Ordovician in North Shuntuoguole area. Notes: nC_3 = n -propane; nC_4 = n -butane; nC_5 = n -pentane; 2-MC $_5$ =2-methylpentane; 3-MC $_5$ =3-methylpentane; nC_6 = n -hexane; MCYC $_5$ =methylcyclopentane; Bz=benzene; CYC $_6$ =cyclohexane; 2-MC $_6$ =2-methylhexane; 3-MC $_6$ =3-methylhexane; 1*c*3-DMCYC $_5$ =1,*cis*,3-dimethylcyclopentane; 1*t*3-DMCYC $_5$ =1,*trans*,3-dimethylcyclopentane; 1*t*2-DMCYC $_5$ =1,*trans*,2-dimethylcyclopentane; nC_7 = n -heptane; MCYC $_6$ =methylcyclohexane; Tol=toluene; 2-MC $_7$ =2-methylheptane; nC_8 = n -octane.

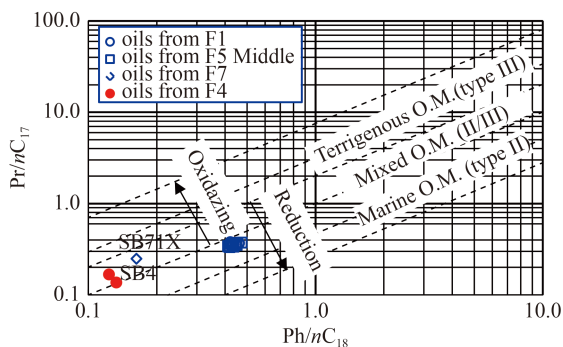


Fig. 3 Pr/nC_{17} vs. Ph/nC_{18} of oil samples from the ultra-deep Ordovician in North Shuntuoguole area, Tarim Basin.

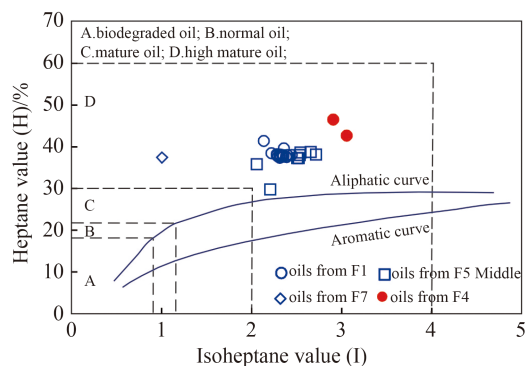


Fig. 4 Heptane value vs. isoheptane value of oil samples from the ultra-deep Ordovician in North Shuntuoguole area, Tarim Basin.

oils from ultra-deep Ordovician in the North Shuntuoguole area ranged 1.14–2.2, suggesting high maturity. Meanwhile, the oil samples from Well SB4 showed the

highest nC_7 /MCH ratio, which values of 1.96–2.47, further indicating that the oil in Well SB4 has the highest maturity.

Table 1 LHs parameters of the ultra-deep Ordovician in the North Shuntuoguole area, Tarim Basin

Fault zone	Well No.	Depth/m	Formation	H/%	I	2-/3-MC ₅	2-/3-MC ₆	K ₁	K ₂	Tol/nC ₇	nC ₇ /MCH	nC ₇ /%	DMCP/%	MCH/%
F1	SB1-3	7274.00–7357.98	O ₂ yj + O ₁₋₂ y	38.02	2.45	1.74	0.87	1.01	0.19	0.34	1.77	53.2	16.7	30.0
	SB1CX	7268.24–7318.70	O ₂ yj + O ₁₋₂ y	41.35	2.14	1.63	0.79	0.91	0.17	0.26	1.79	53.9	16.0	30.1
	SB1-19	7293.87–7421.40	O ₂ yj	39.58	2.36	1.60	0.84	0.95	0.17	0.38	1.72	53.1	16.1	30.8
	SB1-10	7299.50–7768.16	O ₂ yj + O ₁₋₂ y	37.48	2.39	1.78	0.87	1.01	0.19	0.32	1.78	52.9	17.3	29.7
	SB1-18	7301.50–7475.20	O ₂ yj + O ₁₋₂ y	37.60	2.35	1.75	0.85	0.99	0.19	0.34	1.74	52.4	17.4	30.2
	SB1-6	7288.16–7399.75	O ₂ yj	37.57	2.38	1.76	0.86	1.01	0.19	0.33	1.77	52.8	17.3	29.9
	SB1-7	7399.36–7456.00	O ₂ yj	37.89	2.28	1.70	0.83	0.97	0.18	0.31	1.72	52.5	16.9	30.6
	SB1-1H	7458.00–7557.66	O ₂ yj	37.92	2.35	1.78	0.86	1.01	0.19	0.34	1.81	53.4	17.2	29.4
	SB1-23	7495.00–8246.84	O ₂ yj + O ₁₋₂ y	37.61	2.31	1.72	0.84	0.98	0.19	0.32	1.72	52.6	16.9	30.5
	SB1-4	7459.00–7561.96	O ₂ yj	37.60	2.29	1.73	0.84	0.98	0.18	0.30	1.74	52.6	17.1	30.3
	SB1-5	7474.52–7576.19	O ₂ yj	38.44	2.22	1.63	0.81	0.93	0.18	0.32	1.65	51.9	16.6	31.5
	SB1-2	7469.00–7569.47	O ₂ yj	37.62	2.35	1.74	0.85	1.00	0.19	0.32	1.76	52.7	17.3	30.0
	SB1-11	7572.00–7732.17	O ₂ yj	38.16	2.28	1.70	0.83	0.96	0.18	0.30	1.75	52.9	16.9	30.2
	SB1-14	7589.00–7710.00	O ₂ yj + O ₁₋₂ y	37.33	2.31	1.76	0.84	0.98	0.19	0.29	1.75	52.7	17.2	30.1
	SB1-12	7603.00–7648.33	O ₂ yj	37.99	2.34	1.75	0.84	0.98	0.19	0.30	1.79	53.4	16.9	29.7
	SB1-15	7614.00–8007.13	O ₂ yj + O ₁₋₂ y	38.14	2.32	1.70	0.83	0.96	0.18	0.30	1.75	52.9	16.7	30.3
SB1-16	7619.00–7821.50	O ₂ yj + O ₁₋₂ y	37.98	2.40	1.75	0.84	0.98	0.19	0.28	1.80	53.5	16.8	29.7	
F5 Middle	SB51X	7553.64–7876.00	O ₂ yj	29.79	2.21	1.59	0.84	0.96	0.22	0.17	1.14	42.8	19.6	37.6
	SB5-7	7362.80–7635.57	O ₂ yj + O ₁₋₂ y	37.29	2.52	1.78	0.88	1.00	0.20	0.28	1.72	52.8	16.5	30.7
	SB5-5	7630.00–8032.84	O ₂ yj + O ₁₋₂ y	38.61	2.54	1.72	0.87	0.97	0.19	0.31	1.72	53.3	15.7	31.0
	SB501	7628.00–7960.00	O ₂ yj + O ₁₋₂ y	35.82	2.06	1.81	0.83	0.97	0.20	0.23	1.55	49.8	18.0	32.2
	SB52A	7644.00–8137.00	O ₂ yj + O ₁₋₂ y	37.98	2.53	1.78	0.87	0.99	0.20	0.27	1.76	53.6	16.0	30.4
	SB5-10	7639.00–8143.00	O ₂ yj + O ₁₋₂ y	37.28	2.51	1.71	0.86	0.97	0.20	0.27	1.67	52.3	16.3	31.3
	SB5-15	7632.00–7877.63	O ₂ yj + O ₁₋₂ y	38.72	2.66	1.65	0.87	0.95	0.19	0.31	1.69	53.1	15.6	31.3
SB5-6	7514.00–7945.65	O ₂ yj + O ₁₋₂ y	38.12	2.72	1.76	0.90	1.00	0.20	0.31	1.80	54.0	15.9	30.1	
F7	SB71X	7674.00–8024.66	O ₂ yj + O ₁₋₂ y	37.37	1.01	1.68	0.82	0.94	0.15	0.10	1.50	47.9	20.2	31.9
F4	SB4	7771.47–7939.85	O ₂ yj + O ₁₋₂ y	42.63	3.06	1.56	1.04	1.03	0.16	0.89	1.96	55.9	15.7	28.4
	SB4	7771.47–7939.85	O ₂ yj + O ₁₋₂ y	46.48	2.91	1.41	1.09	1.02	0.16	1.03	2.47	59.4	16.5	24.1

Notes: H=nC₇/(CYC₆+2M-C₆+2,3-DMC₅+1,1-DMCYC₅+3-MC₆+1,c3DMCYC₅+1,t3DMCYC₅+3EC₅+1,t2DMCYC₅+nC₇+MCYC₆); I=(2+3-)MC₆/(1,c3+1,t3+1,t2-)DMCYC₅; 2-/3-MC₅=2-/3-methylpentane; 2-/3-MC₆=2-/3-methylhexane; K₁=(2-MC₆+2,3-DMC₅)/(3-MC₆+2,2-DMC₅); K₂=P₃/(P₂+N₂), P₃=2,2-DMC₅+2,4-DMC₅+2,3-DMC₅+3,3-DMC₅+3E-C₅; P₂=2-MC₆+3-MC₆; N₂=1,1-DMCYC₅+1,c3-DMCYC₅+1,t3-DMCYC₅; Tol/nC₇=toluene/heptane; nC₇/MCH=n-heptane/methylcyclohexane; nC₇=n-heptane; DMCP=(1,1-+1c3-+1t3-+1t2-) dimethylcyclopentane; MCH=methylcyclohexane.

Berment et al. (1995) proposed that the 2,4-DMP/2,3-DMP ratio is a function of temperature and can be used to predict the formation temperature of oil. Mango (1987, 1990, 1997) suggested the equation of T (°C) = 140 + 15×ln(2,4-/2,3-DMP) to calculate the formation temperature of oil. The formation temperatures of the Ordovician oils in the North Shuntuoguole area ranged from 118.8°C to 126.8°C. Generation temperature of oils from F1 ranged 120.6°C–123.7°C (averaging at 122.6°C), except for the oil from Well SB1CX, which was 118.8°C. Generation temperatures of oils from F5 Middle and oil from F7 were 123°C–126.8°C (averaging at 125.2°C) and 119.5°C, respectively. For the two oil samples collected in different time from Well SB4, the generation

temperatures were consistent with values of 126.6°C–126.8°C and 126.7°C on average. Therefore, the generation temperature of the samples from different faults was in the order of F7 < F1 < F5 Middle < F4.

Oil maturity is an obscure concept, because the oil is a mixture of multiple charged oils with different maturity. Moreover, different maturity indexes have their own valid range. Due to low concentrations of biomarkers in the oils, the biomarker maturity parameters, such as C₃₁ hopane 22S/(22S+22R), C₂₉ sterane 20S/(20S+20R) and C₂₉ sterane ββ/(ββ+αα) are not effective (Ma et al., 2020). As calculated by methyl adamantane index (MAI) and methyl diamantane index (MDI), the equivalent vitrinite reflectance of the oil samples from different faults in

North Shuntuoguole area is 1.3%–1.6% (Ma et al., 2021), which is basically consistent with the oil maturity calculated by the heptane and isoheptane values, but differs from maturity obtained based on aromatic hydrocarbon parameters to some extent (Ma et al., 2020, 2021). As indicated by the methyl phenanthrene index (MPI1) and methyl phenanthrene ratio (F_1), the maturity of F1 and F5 Middle was 1.00%–1.08% and that of F7 was 0.7%–0.80% (Ma et al., 2021). Zhang et al. (2005) and Ma et al. (2017) suggested that the difference in maturity derived from different parameters resulted from multi-stage charging. According to Chang et al. (2014), the hydrocarbon in Halahatang area in Tarim Basin were charged by two stages, and the heptane and isoheptane values only represented the maturity of the late charged oil. As far as the multiple charged oil reservoir is concerned, the late charged more mature oil generally had more light hydrocarbons than the early charged oil. In North Shuntuoguole area, the oil maturity calculated by the LHs and diamondoids parameters may reflect the maturity of late charged oil.

4.3 Biodegradation

Biodegradation is the most common secondary alteration of oil reservoirs (Tissot and Welte, 1984). The formation of the Ordovician heavy oil in Tahe and Lunnan Oilfields in Tarim Basin is related to biodegradation occurring in the late Hercynian period (Zhang et al., 2014). Biodegradation generally takes place in shallow-buried reservoirs with a temperature below 80°C (Larter et al., 2003). The Ordovician oil in North Shuntuoguole area mostly consists of light oil and volatile oil, with no 25-norhopane detectable, indicating low biodegradation degree (Cao et al., 2020).

Biodegradation degree can be reflected by the relevant ratios of LHs. The resistance to biodegradation of 2-MC₅ and 2-MC₆ is lower than that of 3-MC₅ and 3-MC₆. Therefore, the irrelevant ratio decreases with an increase in biodegradation. Compared with iso-alkanes, *n*-alkanes are prone to biodegradation. Therefore, the relevant ratio of iC_5/nC_5 and 3-MC₅/ nC_6 increases with an increase in

biodegradation (Welte et al., 1982; Harris et al., 2003; Yang et al., 2015).

The oil samples from Ordovician in North Shuntuoguole area show relatively high 2-/3-MC₅ and 2-/3-MC₆ ratios of 1.41–1.81 and 0.79–1.09, respectively (Fig. 5) and relatively low iC_5/nC_5 and 3M-C₅/ nC_6 ratios of 0.31–0.90 and 0.16–0.37, respectively. However, two Ordovician biodegraded oil samples from Aiding (AD) block of Tahe Oilfield have relatively low 2-/3-MC₅ and 2-/3-MC₆ ratios of 1.55–1.61 and 0.49–0.51, respectively, and relatively high iC_5/nC_5 and 3-MC₅/ nC_6 ratios of 0.90–0.98 and 0.35–0.46, respectively. This indicates that the oils in North Shuntuoguole area have not experienced biodegradation.

Biodegradation can reduce the heptane and isoheptane values of oil (Thompson, 1983; Wang et al., 2010). The oil samples from different faults in North Shuntuoguole area showed high and dispersedly distributed heptane and isoheptane values, indicating that oil in the area has suffered little biodegradation.

The Ordovician Yijianfang and Yingshan Formations (O_{2y}+O_{1–2y}) oil reservoirs in North Shuntuoguole area lack the geological conditions for biodegradation. The strata above the oil reservoirs included Qia'erbake (O_{3q}), Lianglitage (O_{3l}) and Sangtamu (O_{3s}) Formations of Upper Ordovician, Kepingtage (S_{1k}), Tata'ai'ertage (S_{1t}) Formations of Lower Silurian, with thickness greater than 1800 m before the sedimentation of Yimugantawu Formation (S_{2y}). Although Yimugantawu Formation (S_{2y}) of Middle Silurian was eroded completely at the end of Late Caledonian, due to the capping of mudstone with thickness ranging 700–1000 m of Sangtamu Formation (O_{3s}), the Ordovician reservoirs was unsusceptible to biodegradation. Xiaohaizi Formation (C_{2x}) of Upper Carboniferous was eroded at the late Hercynian, the mudstone of Bachu Formation (C_{1b}) of Lower Carboniferous could act as another cap rocks for the reservoirs in the late Hercynian period.

4.4 TSR

TSR refers to the process in which petroleum hydrocarbons

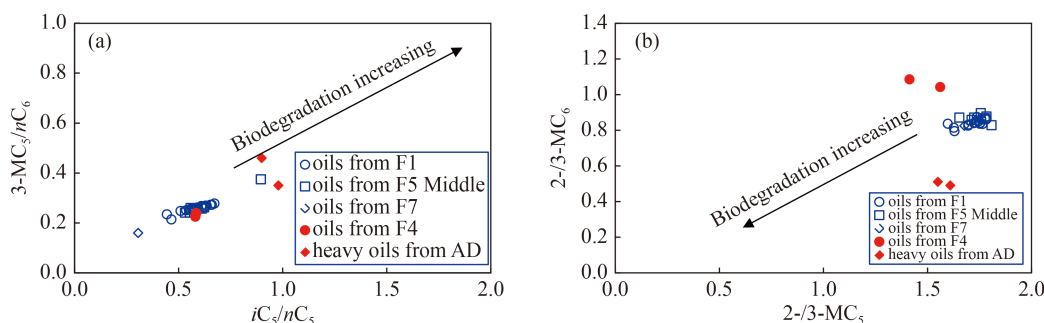


Fig. 5 (a) 3-MC₅/ nC_6 vs. iC_5/nC_5 and (b) 2-/3-MC₆ vs. 2-/3-MC₅ of oil samples from the ultra-deep Ordovician in the North Shuntuoguole area, Tarim Basin.

react with inorganic sulfate to produce CO_2 , H_2S , and solid asphalt in gypsum-bearing and gypsum mudstone strata in high-temperature reservoirs (80°C – 200°C). Oil can be fully oxidized to CO_2 and H_2S under extreme conditions (Worden et al., 1995).

According to Wang et al. (2005), the oil in saline-lake basins has a K_1 value of 1.32–1.73 and 1.42 on average and high toluene content and thus in saline-lake environment, the rate of *n*-heptane converting to 2-methylhexane is higher than that of *n*-heptane converting to 3-methylhexane, leading to the higher K_1 value of the oil. Mango (1997) suggested that the K_1 value of the oil suffered TSR tends to significantly increase. In this study, the Ordovician oil samples from North Shuntuoguole area had a light hydrocarbon ratio K_1 of 0.91–1.03 (Fig. 6(a)), indicating weak TSR. Song et al. (2017) proposed that the oils altered by TSR in Well TZ4 in Tazhong area of Tarim Basin generally have K_1 ratios greater than 1.26 and high concentrations of dibenzothiophenes (DBTs). In this study, the Ordovician oil samples from North Shuntuoguole area had a wide range of C_0 – C_3 DBTs concentrations of 182–2412 $\mu\text{g/g}$. Specifically, the oil samples of Well SB71X from F7 had the lowest DBTs concentrations of 182 $\mu\text{g/g}$, those from F4 had much higher DBTs concentrations of 1558–2412 $\mu\text{g/g}$, and those from the F5 Middle and F1 showed DBTs concentrations of 880–1714 $\mu\text{g/g}$ (Fig. 6(b)). Therefore, the oils in F1, F5 Middle, and F7 have not suffered TSR roughly, while the oil in Well SB4 has experienced slight TSR according to their DBTs concentrations.

From the thiadiazole concentrations in the oil and the H_2S content in the natural gas, it can be verified that the oil in the Well SB4 has experienced slight TSR. The oil samples from Well SB4 had thiadiazole concentrations of 42.1–76.9 $\mu\text{g/g}$, while other oil samples had thiadiazole concentrations of 0–19.59 $\mu\text{g/g}$ (Ma et al., 2020). Cai et al. (2016) proposed that the threshold for occurring TSR should be set as the thiadiazole concentrations of 28 $\mu\text{g/g}$, and Ma et al. (2018) pointed out that the thiadiazole concentrations in oil above 80 $\mu\text{g/g}$ indicates notable TSR. In this study, the natural

gas from Well SB4 had comparatively high H_2S content of 17759–82806 mg/m^3 and 53738 mg/m^3 on average, also indicating the occurrence of slight TSR in the reservoirs.

From the observation of core of well SB4, no pyrobitumen, gypsum-bearing and gypsum mudstone were developed in the interval of Ordovician, lacking geological conditions for *in-situ* TSR. However, the deep Cambrian, with two sets of salt rock caps, Awatage (C_2a) and Wusonggeer (C_1w) Formations developing, might be more suitable for TSR because sulfate or the related salt brine is one of the most important requirements for TSR (Cai et al., 2016). It is proposed that the TSR-altered H_2S and oil of well SB4 were migrated from the deep Cambrian.

4.5 Evaporative fractionation

Evaporative fractionation refers to the processes that the gases are separated from saturated gas-bearing oil to form a gas cap due to the pressure drop of the reservoirs induced by tectonic uplift and denudation or fault activities and then, affected by geological factors such as fault activities, gases dissolve out of the gas cap and migrate upward to a suitable trap to form condensate oil reservoirs while carrying the low molecular weight compounds (Thompson, 1987, 1988, 2010; Zhang et al., 2011).

The secondary alteration suffered by oil can be characterized by the ratios of toluene to heptane and the *n*-heptane to MCH. Oil experienced evaporative fractionation tends to have a high toluene/*n*-heptane ratio and a low *n*-heptane/MCH ratio (Thompson, 1987, 1988, 2010). In this study the oil samples from Well SB4 in F4 had a high toluene/*n*-heptane and *n*-heptane/MCH ratios, with values of 0.89–1.03 and 1.96–2.47, respectively. In contrast, other oil samples from North Shuntuoguole area showed low toluene/*n*-heptane and *n*-heptane/MCH ratios of 0.10–0.38 and 1.50–1.80, respectively (averaging at 0.29 and 1.71, respectively; Fig. 7). This is consistent with the study results of Cheng et al. (2020), who states that the toluene/*n*-heptane and *n*-heptane/MCH ratios of the oil in North Shuntuoguole area are 0.08–0.36 and 1.41–1.81, respectively.

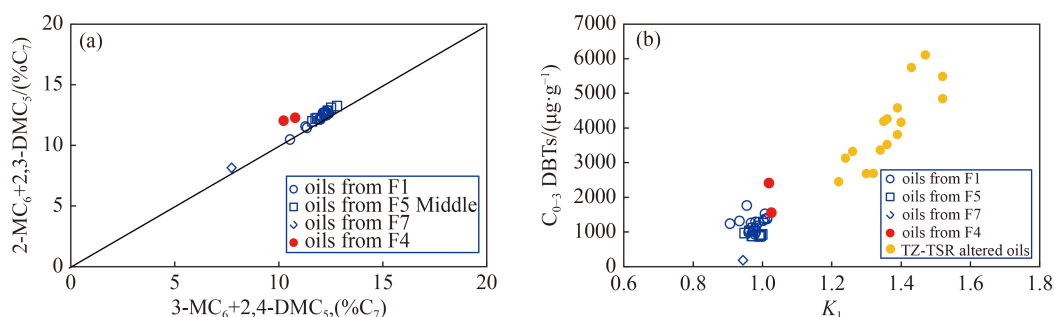


Fig. 6 3- $\text{MC}_6 + 2,4\text{-DMC}_5$ vs. 2- $\text{MC}_6 + 2,3\text{-DMC}_5$ and (b) K_1 vs. C_0 – C_3 DBT content of oil samples from the ultra-deep Ordovician in North Shuntuoguole area, Tarim Basin.

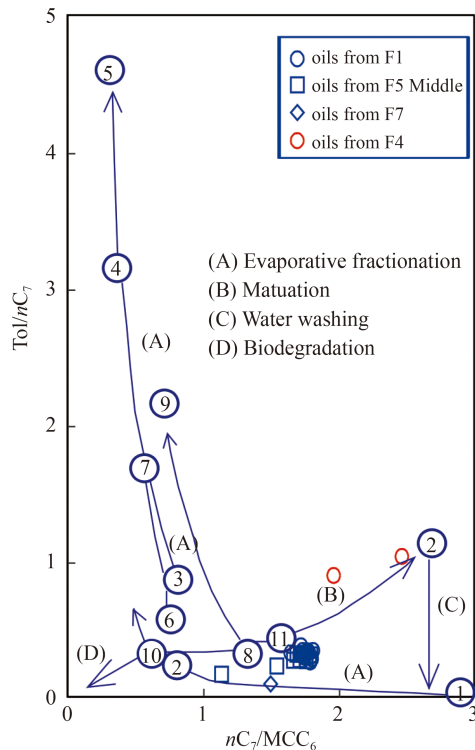


Fig. 7 Toluene/ nC_7 vs. nC_7/MCC_6 of Ordovician oil samples of ultra-deep Ordovician from North Shuntuoguole area, Tarim Basin.

High-mature, unaltered oils have toluene/ nC_7 ratio of 0.20–0.50, with an average value of 0.25 (Thompson, 1987). Low value of toluene/ nC_7 ratios in the most oils studied suggested that they did not suffered notable evaporative fractionation except for the oil from Well SB4, which fell on the evolution curve of maturation. According to Zhang et al. (2011), the toluene/ nC_7 and $nC_7/MCYC_6$ ratios of the oil from the Ordovician in the Lunnan area are 0.20–0.80 and 0.75–1.75, respectively, and the waxy oil in the Lunnan area experienced evaporative fractionation. From the ratios of toluene/ nC_7 and nC_7/MCH of the oil in the Ordovician and relationship between the mole fraction of n -alkanes in oils and carbon number of n -alkanes in the whole oil chromatograms, Chai et al. (2020) proposed that the Ordovician oil in F1 in North Shuntuoguole area

has experienced evaporative fractionation and the oils in F5 has suffered no evaporative fractionation.

4.6 Oil family and sources rocks

4.6.1 Oil family

Different types of oils in Tarim Basin differ greatly in the K_2 value. In general, marine oils have a relatively low K_2 value of 0.20–0.23 on average, while terrigenous oils have a relatively high K_2 value of 0.29–0.36 on average (Zhu et al., 1999; Zhang et al., 1999). In this study, the oil samples from North Shuntuoguole area showed a K_2 value of 0.15–0.22, indicating that the oil in the Ordovician in the area is marine oil.

The oils of different origins can be distinguished using the MCH index (Hu et al., 1990; Lin et al., 1998). MCH indexes for marine, lacustrine, mixed-source and coal-derived oils are in range of < 35%, 35%–50%, 50%–65%, and > 65%, respectively (Lin et al., 1998). All the oil samples from North Shuntuoguole area showed a MCH index of < 35%, indicating typical light hydrocarbon composition of marine oils.

Mango (1990) proposed the steady-state catalytic process to explain the genesis of C_7 hydrocarbons in oils and established the kinetic mode for the formation of C_7 hydrocarbons. Mango (1992) compared and classified oil based on the relationship between P_3 and $(P_2 + N_2)$ and the relationship between the P_2 content in C_7 hydrocarbons and N_2/P_3 ratio, achieving satisfied effects. Zhang (1999) distinguished the marine and lacustrine oils in Tarim Basin based on P_2-P_3/N_2 and $nC_7-1,2-DMC5(c,t)/MCH$ ratios. In this study, there existed a good positive correlation between P_3 and $P_2 + N_2$ and a negative correlation between P_2 and N_2/P_3 of the LHs in the oil samples from North Shuntuoguole area (Fig. 8), with correlation coefficients R^2 of 0.8053 and 0.8807, respectively, further indicating that the oils from different Ordovician faults in North Shuntuoguole area shared the same hydrocarbon source rocks.

LHs derived from sapropelic-type parent materials are rich in n -alkanes, while LHs derived from humic-type

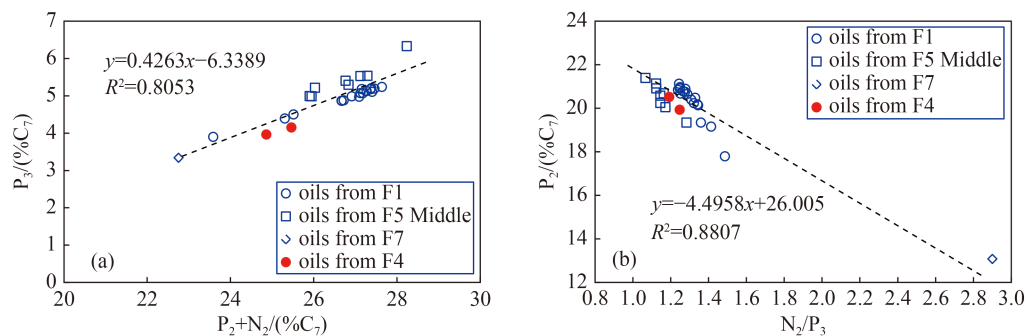


Fig. 8 (a) P_3 vs. $(P_2 + N_2)$ and (b) P_2 vs. N_2/P_3 of LHs in Ordovician oil samples from North Shuntuoguole area, Tarim Basin.

parent materials are rich in iso-alkanes and aromatic hydrocarbons (Leythaeuser et al., 1979). Snowdon and Powell (1982) proposed that the condensate oil rich in naphthenes is an important characteristic of terrigenous parent materials. The composition of C_{5-7} LHs can identify parent material types (Hu et al., 1990). According to the diagram of C_{5-7} light hydrocarbon composition in this study, the oil samples from North Shuntuoguole area mainly consisted of *n*-alkanes, followed by iso-alkanes and cycloalkanes, which had approximate content. In detail, the nC_{5-7} -*n*-alkanes, iso-alkanes, and naphthenes in oil samples accounted for 33.12%–45.18%, 19.87%–32.91%, and 23.21%–30.85% (Fig. 9(a)), respectively, indicating the organic matters of the oils in North Shuntuoguole area dominated by sapropelic-type organic matter.

The genetic types of oils can be determined using a triangle diagram of nC_7 , dimethylcyclopentane (DMCYC₅), and MCH (Hu et al., 1990). In C_7 compounds, nC_7 is mainly sourced from algae and bacteria, MCH mainly from advanced lignin, cellulose, and sugar, and DMCYC₅ from lipids of aquatic organisms (Hu et al., 1990). The C_7 LHs of oil samples from North Shuntuoguole area, were dominated by paraffins, with nC_7 accounting for 42.83%–59.39%, followed by MCH, with values of 24.07%–37.61%. Meanwhile, C_7 LHs showed low DMCYC₅ contents of 15.71%–20.91% and roughly < 20% (Fig. 9(b)). The relatively high nC_7 content in C_7 compounds suggested that the source rocks are dominated by algae and bacteria.

4.6.2 Source rocks

The main marine source rocks in the platform area of Tarim Basin have been in dispute for a long time (Zhang et al., 2000; Cai et al., 2015; Huang et al., 2016; He et al., 2020, 2022). At present, both the Sinopec Northwest

Oilfield Company and Tarim Oilfield Company of PetroChina consider that the black shales of the Lower Cambrian Yu'ertusi Formation serve as main marine source rocks in the platform area mainly according to high single-well production of wells near strike-slip faults connecting Cambrian source rocks (Liu, 2020), the carbon and sulfur isotopes of oils (Cai et al., 2015), and aryl isoprenoids (Sun et al., 2003; Huang et al., 2016; He et al., 2020, 2022).

Due to relatively high maturity, the concentration of aryl isoprenoids of oil samples in North Shuntuoguole area is generally low. In the aromatic fraction of oil of well SB53X, complete aryl isoprenoids series ranging from C_{11} to C_{24} were detected (Fig. 10). Compared with the aryl isoprenoids of heavy oil from well AD 4 from Aiding Block of Tahe Oilfield, the distribution of aryl isoprenoids of oil from well SB53X decreased sharply from C_{13} . More importantly, completely aryl isoprenoids series were also detected in the source rocks of Yu'ertusi Formation of Lower Cambrian (He et al., 2022), further showing the genetic relationship between Ordovician ultra-deep oils in North Shuntuoguole area and Cambrian Yu'ertusi Formation source rock.

Song et al. (2016) distinguished Cambrian-Lower Ordovician oils from Middle-Upper Ordovician oils using the triangle diagram formed from LHs. In detail, the former is relatively rich in naphthenes, while the latter is relatively rich in *n*-alkanes and has a high *n*-heptane/MCH ratio and high aromatic hydrocarbon content (benzene and toluene). Meanwhile, the oil from the Lower Cambrian Xiao'erbulake Formation in Well ZS1C clustered with the Middle-Upper Ordovician sourced oils. Song et al. (2016) proposed that the rich naphthenes in the Cambrian-Lower Ordovician oils may be related to the rich clay minerals in Cambrian-Lower Ordovician source rocks.

According to the composition of LHs in nC_{5-7} and C_7

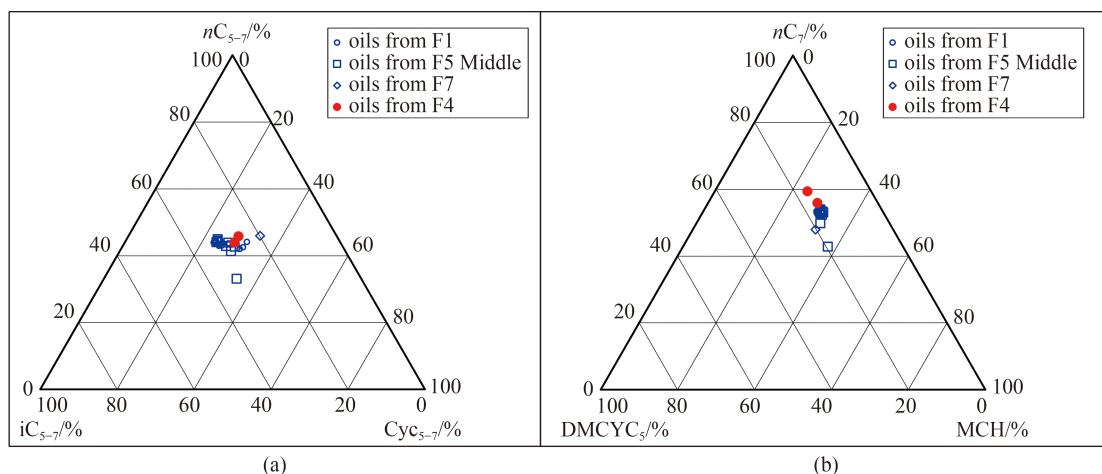


Fig. 9 Triangle diagrams of LHs of oil samples from the Ordovician in North Shuntuoguole area, Tarim Basin. (a) Triangle diagram of nC_{5-7} , iC_{5-7} and CyC_{5-7} ; (b) Triangle diagram of nC_7 , DMCYC₅ and MCH.

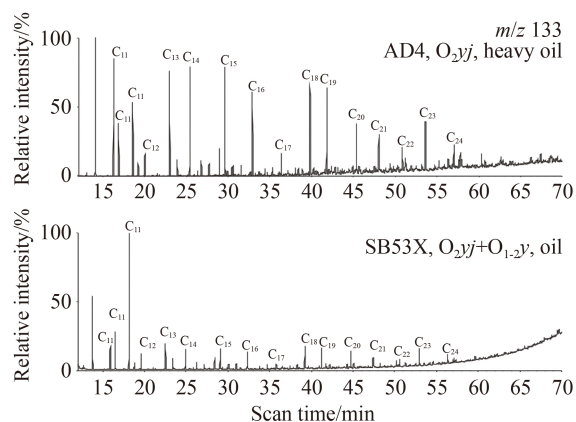


Fig. 10 Mass chromatograms of aryl isoprenoids of oil samples from wells AD4 and SB53X.

(Fig. 9), the oil samples in different Ordovician faults in the area were rich in *n*-alkanes series. This is the same as the light hydrocarbon distribution of the Ordovician oils in the Halahatang Sag (Cheng et al., 2013; Chang et al., 2014), the shallow Cretaceous oils in Tahe Oilfield, the Cretaceous and Triassic oils in Yuqi area (Chang et al., 2014).

As shown in the Pr/*n*C₁₇-Ph/*n*C₁₈ plot (Fig. 3), the organic matters of the oil samples from the area were marine type II organic matter except for the oil samples from Wells SB71X and SB4, which were mixed type II/III organic matter. As shown in the Pr/Ph-DBT/P plot (Ma et al., 2020), the oil in Ordovician from F1 in the area fell into the junction of marine carbonate rocks, marine shales, and lacustrine super saline environment, while the oil in F7 fell into the marine shale/mudstone area. Since a lacustrine super-saline environment had not developed in the platform area, the Ordovician oil in the area mainly originated from marine shales/mudstones, which mainly corresponds to the source rocks of the Cambrian Yu'ertusi Formation. Meanwhile, the organic facies of source rocks may slightly differ in different fault zones from the LHs, biomarker and aromatic parameters.

5 Conclusions

1) The heptane and isoheptane values of the oil samples from Ordovician in North Shuntuoguole area were 29.79%–46.86% and 1.01–3.06, respectively, suggesting high maturity. According to the isoheptane value, the oil maturity was in the order of F7 < F1 < F5 Middle < F4. Meanwhile, the oil maturity calculated based on the heptane and isoheptane values was higher than that calculated using aromatic hydrocarbon parameters. Therefore, the former mostly reflects the maturity of the late charged oils.

2) As indicated by the low *i*C₅/*n*C₅ and 3-MC₅/*n*C₆ ratios and high 2-/3-MC₅ and 2-/3-MC₆ ratios of the LHs

in the oil samples, the oils in Ordovician in North Shuntuoguole area have not experienced biodegradation. The *K*₁ value of the LHs in the oil samples was about 1.0, indicating that most of the oils have not suffered TSR. Meanwhile, the low toluene/*n*C₇ and *n*C₇/MCH ratios of the oil samples indicate that the oil reservoirs in the area have not experienced notable evaporative fractionation.

3) There was a high positive correlation between P₃ and P₂ + N₂ and negative correlation between P₂ and N₂/P₃ of the oil samples from Ordovician in North Shuntuoguole area, indicating that the oils in Ordovician share the same genesis. The oil samples were rich in *n*-alkanes series. The detection of complete aryl isoprenoids in the oils from North Shuntuoguole area further suggested that oils were originated from the source rocks of Lower Cambrian Yu'ertusi Formation. However, the source rocks in different fault belts slightly differ in organic facies.

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