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Total alkyl dibenzothiophenes content tracing the filling pathway of condensate reservoir in the Fushan Depression, South China Sea

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The condensates are generally characterized by high maturity, low concentration of steranes and terpanes biomarkers and low content of non-hydrocarbon fraction. In this case commonly used steranes, terpanes and carbazoles parameters cannot be effectively applied in the reservoir-filling tracing. The hydrogen bond formed by sulfur atom in the dibenzothiophenes (DBTs) results in molecule adsorption and fractionation during oil migration in reservoir. Like carbazoles, total DBTs content decreases with the increasing of oil migration distance. Therefore, a new parameter——total DBTs content is proposed to be used to trace the oil migration orientation and filling pathway. In present study, total DBTs contents of condensates and light oils are obtained by adding internal standard——eight deuterium atoms substituted DBT during Gas Chromatography-Mass Spectrometry analysis of aromatic fraction. Except for a few samples with much lower content of non-hydrocarbon fraction, the total DBTs content shows a fine positive correlation with that of carbazoles. Large errors can be caused in the process of pyrrolic nitrogen compounds separation. The application of this new parameter in the Fushan Depression of Beibu Gulf Basin, South China Sea indicates that this parameter is a reliable one to trace filling pathway in condensate reservoirs. Combined with other DBTs-related parameters, such as 4-/1-methydibenzothiophene and 2,4-/1,4-dimethyldibenzothiophene, oil migration orientation and filling pathway of the Fushan Depression was determined. The accumulations of Huachang oil field in the Fushan Depression are mainly migrated and charged from northeast to southeast along the Huachang uplift. It can be predicated that the light oil and condensates in the Huachang oil field should be sourced from the source kitchen at the Bailian Sag. It shows that total DBTs content is an effective parameter to tracing oil migration orientation and filling pathway.

dibenzothiophene, alkyl dibenzothiophene, condensate reservoir, filling pathway, molecular markers, the Fushan Depression

England et al.[1,2] first established a filling model of petroleum in sandstone reservoir, providing a scientific theory basis for reconstruction of oil migration pathways and orientation, definition of filling point and potential source kitchen as well as predication of "satellite reservoir" based on the differences of oil maturity, the oil/gas ratio, oil physical properties, etc. Since then, the focus of the petroleum geochemists has moved from exploration and increasingly towards production and reservoir-related problems.

Reservoir geochemistry has been developed and successfully applied in the petroleum exploration, reservoir appraisal and production monitoring[2], but some limitations have been met in condensate and light oil reser-

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voirs. Generally, the condensates have the following characteristics: 1) high maturity; 2) low density and low content of asphaltenes and non-hydrocarbon fraction; 3) low concentration of steranes and terpanes. Higher-molecular-weight components, including the biomarkers, occur in low concentration or are absent in many condensates[3]. Some biomarkers, such as C_{29}-sterane isomerization ratios, are not useful for samples showing maturities beyond peak oil generation ($R_o \sim 0.9\%$) because the reactions they present have reached equilibrium[4]. So these ratios cannot indicate the maturity differences within condensate samples. Furthermore, low concentrations of biomarkers may introduce analytical difficulties for their low signal-noise ratios in Gas Chromatography-Mass Spectrometry (GC-MS) analyses and obscure the application of frequently-used geochemical parameters[3]. Low concentration of pyrrolic nitrogen compounds in condensates may also result in inaccurate total carbazole content.

As heterocyclic aromatic hydrocarbons, the dibenzothiophenes (DBTs) and its alky derivatives are commonly regarded as aromatic sulfur compounds (ASC) in recent literatures. These compounds can be detected in the aromatic fraction of crude oil and sediment bitumen in regular GC-MS analysis[5−10]. Up to present, the molecular markers of alkyl DBTs were mainly applied in the study of maturity assessment[6−13], sedimentary environments[5,14,15], or source rock types[16]. However, Wang et al.[17] pointed out that some of the dibenzothiophenes maturity indicators, such as 4-/1-methyldibenzothiophene (4-/1-MDBT), 2,4-/1,4-dimethydibenzothiophene (2,4-/1,4-DMDBT), and 4,6-/1,4-dimethyldibenzothiophene (4,6-/1,4-DMDBT) can also be used as molecular tracers in definition of oil filling orientation and migration pathway. These parameters have been successfully applied in sandstone reservoirs or carbonate pore-fissure-network karst reservoir.

The theory that molecular parameters of alkyl DBTs can serve as tracing indices for oil migration orientation and filling pathways is that both molecular thermodynamic stability and hydrogen bond mechanism will result in identical distribution of alkyl DBT molecules. However, so far there still is no report on the migration fractionation resulting solely from migration fractionation of alkyl DBTs. In the present study, the authors got the absolute concentrations of DBTs and alkyl DBTs by adding internal standard-eight deuterium atoms substituted DBT in the condensate and light oil samples from the Fushan Depression, Beibu Gulf Basin, South China Sea. Therefore, the migration fractionation of DBTs can be studied and a new DBTs-related tracing parameter can be established.

1 Experimental and methods

Condensates and light oil samples were treated with routine analytical procedure. Oil was deasphalted by *n*-hexane, and then aliphatic and aromatic fractions were isolated by liquid chromatography on silica gel and alumina column using *n*-hexane and dichloromethane as eluents.

GC-MS of the aromatic fraction has been performed on a Finnigan Model SSQ-710 quadrupole analytical system coupled with a DB-5 fused silica capillary column (30 m×0.32 mm i.d.) and an IAIS data processing system. GC operating conditions: temperature program was, initial at 80℃ for 1 min, ramped to 300℃ at 3℃/min, and then isothermal for 15 min, Helium as a carried gas. Injector temperature was set at 300℃. MS conditions: electron ionization (EI) mode, electron energy 70 eV, emission current 300 μA, and scanning range *m*/*z* 50－600.

The pyrrolic nitrogen fraction was separated by "two-stage isolation method"[18−21]. GC/MS of the pyrrolic nitrogen fractions was performed by using a Thermal Finnigan Trace-DSQ spectrometer combined with a gas chromatograph equipped with a 30 m fused silica capillary column (HP-5MS, 0.25 mm i.d., 0.25 μm film thickness). The GC oven was initially at 80℃ for 1 min, then ramped to 150℃ at 15℃/min and to 270℃ at 3℃/min with a final hold of 10 min. The mass spectrometer was operated in selective ion monitoring (SIM), electron impact modes with electron energy of 70 eV.

In comparison with the relative retention time on *m/z* 184, 198, 212 and 226 mass chromatograms published by previous authors[7,8,22]. DBT, MDBTs, DMDBTs, and TMDBTs (trimethyldibenzothiophenes) can be assigned and confirmed in the samples analyzed (Figure 1). Eight deuterium atoms substituted DBT ($C_{12}D_8S$) are eluted in the samples during GC-MS analysis. The peak of $C_{12}D_8S$ can be identified on *m/z* 192 mass chromatograms, which is just eluted before the methyl phenantharene peaks (Figure 1). By correlation with the peak

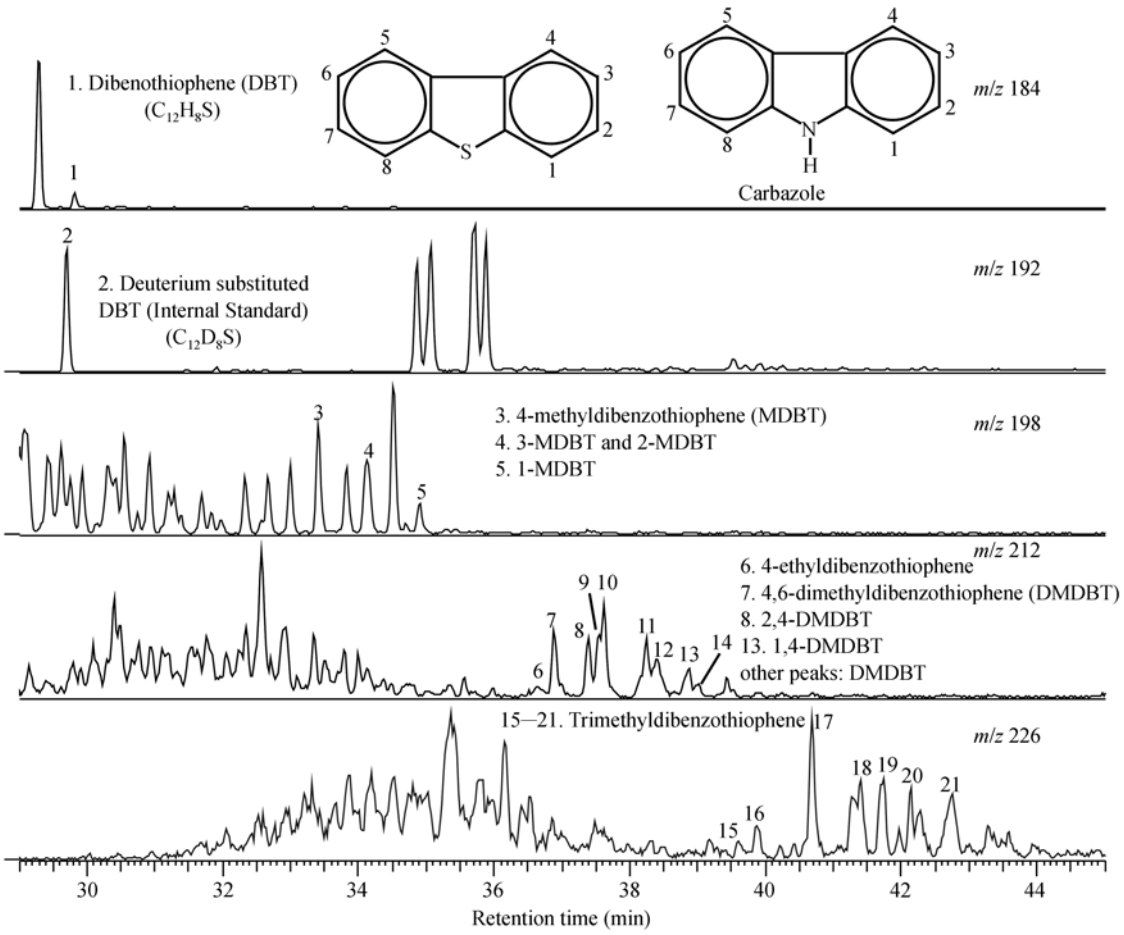

Figure 1 Identification of DBTs on mass chromatograms and molecular structures of DBT and Carbazole.

area of $C_{12}D_8S$, the absolute total DBT and alkyl DBTs content can be calculated.

2 Results and discussion

2.1 Molecular structure and chemical properties

The molecular skeleton of DBT is composed of two benzene rings and a five-membered thiophenic ring (Figure 1). The symmetric molecular structure of DBT enables its skeleton to have properties of high thermodynamic stability and strong anti-biodegradation. Due to their molecular thermodynamic stability, DBTs with alkyls substituted at different positions show diverse levels of thermodynamic stability, i.e. 1-position is less stable than the 3-position which is less stable than the 2-position, and 4- and 6- positions are more stable[8]. In the light of previous studies, relative distributions of methylated aromatic compounds are thermodynamically controlled and related to the enthalpy of formation. The lower the value of the enthalpy of formation, the greater the stability of that compound[8]. According to the values of enthalpy of formation of DMDBTs[23], the stability of 1,4-DMDBT is similar to that of 2,4-DMDBT, which is much less than 4,6-DMDBT. With increasing of maturity, alkyl DBT molecular parameters, i.e. the 4-/1-MDBT, 2,4-/1,4-DMDBT and 4,6-/1,4-DMDBT ratios, should be elevated due to the increasing of the amount of thermostable isomers[8].

In view of the reservoir filling model established by England et al.[1], oil migration orientation and filling pathways can be characterized by the subtle change of oil maturity parameters within a reservoir scope, the difference of maturity or the concentration of some compounds is mainly controlled by the oil filling time and migration fractionation. Early-filled oil shows a lower maturity level than that of late-filled one, and relatively the most mature oil is situated near the filling point of the reservoir. Therefore, alkyl DBT molecular parameters can also serve as tracers for reservoir filling process.

In carbazoles, a hydrogen bond can be formed by interaction between its N-H functional group and the negative electric atom in organic matter or in hydroxyl group on the surface layer of clay minerals, resulting in molecular adsorption and fractionation of carbazole isomers during oil migration in reservoir, which can trace the oil migration orientation and filling pathway[19−21,24,25]. The molecular skeleton of DBTs is similar to that of carbazole, but the five-membered heterocyclic in DBTs is S-containing thiophenic ring, instead of an N-containing pyrrolic ring (Figure 1). By means of uncoupled lone-pair electrons of S atom, the hydrogen bond of thiopenic ring in DBTs can also be formed with circumferential medium. Therefore, the alkyl DBT molecules would be adsorbed by hydrogen bond on the medium, resulting in oil migration fractionation as well[17].

2.2 Total DBTs content: a new parameter tracing condensate reservoir migration orientation and filling pathway

As discussed above, the decreasing of 4-/1-MDBT, 2,4-/1,4, and 4,6-/1,4-DMDBT ratios along the oil filling pathway is not only contributed by the differences of maturity, but also by the migration fractionation. The degrees of migration fractionation cannot be determined by these parameters. The absolute concentration of DBTs can be used to determine the degree of migration fractionation, and the related parameters can be established to trace the migration orientation and filling pathway in oil or condensates reservoirs.

A total of 22 light oil and condensate samples are collected from the Fushan Depression, Beibu Gulf Basin, South China Sea. The density of these samples is commonly lower than 0.8000 $g \cdot cm^{-3}$, with a minimum of 0.7610 $g \cdot cm^{-3}$ (Table 1). The non-hydrocarbon fraction is as lower as 4.0%, with a minimum of not more than 1.0%. The maturity estimated by MPI (methyl phenantharene indices) is relatively higher, with an equivalent R_o of 0.9%—1.1%[26]. In some light oils and condensates, e.g. wells H7 and Hd1-1, some biomarkers, especially steranes cannot be identified in the mass chromatograms of saturate fraction for their poor signal/noise ratios. Therefore, some frequently-used molecular parameters are difficult to obtain.

In this study, the absolute total DBTs and carbazoles contents in all light oils or condensates are obtained and

Table 1 Properties of oil samples in the Fushan Depression and selected molecular parameters for filling pathway tracing[a)]

Sample No.	Well	Fm.	Density ($g \cdot cm^{-3}$)	S ($mg \cdot g^{-1}$)	N ($mg \cdot g^{-1}$)	[a]/([a]+[c])	Ts/(Ts+Tm)	Aromatics (%)	Non (%)	MDR	4,6-/1,4-	2,4-/1,4-
FY-H1-(03)	H1	E_2l_3	0.7918	0.319	0.124	0.63	0.67	14.21	5.46	8.31	2.13	1.81
FY-H1-1-(01)	H1-1	E_2l_3	0.8297	0.232	0.097	0.63	0.90	16.28	4.65	8.03	2.23	1.55
FY-H2	H2	E_2l_3	0.7868	0.111	0.049	0.58	0.75	8.47	3.39	7.41	1.89	1.59
FY-H2-1	H2-1	E_2l_3	0.7828	0.251	0.104	0.61	0.85	22.55	3.92	6.10	1.98	1.37
FY-H2-2	H2-2	E_2l_3	nd	0.201	0.112	0.62	0.77	31.25	3.91	5.67	1.89	1.50
FY-H2-3	H2-3	E_2l_3	0.7791	0.101	0.052	0.63	0.77	14.90	3.85	9.26	3.07	2.33
FY-H3	H3	E_2l_3	0.7789	0.222	0.096	0.63	0.75	13.68	4.25	6.69	1.68	1.41
FY-H3-1	H3-1	E_2l_3	0.7965	0.298	0.134	0.63	0.86	26.41	3.73	6.93	1.99	1.55
FY-H3-2	H3-2	E_2l_3	0.7881	0.193	0.145	0.63	0.81	21.21	1.82	6.08	1.52	1.23
FY-H3-3	H3-3	E_2l_3	0.7896	0.336	0.149	0.63	0.81	18.60	6.40	5.85	1.66	1.46
FY-HX4-(01)	Hx4	E_2l_3	0.7687	0.171	0.062	0.57	0.73	13.22	8.05	5.04	1.37	1.11
FY-HX4-(02)	Hx4	E_2l_3	0.8251	0.190	0.084	0.61	0.72	12.63	3.68	5.14	1.27	1.08
FY-HX4-(03)	Hx4	E_2l_3	0.8128	0.083	0.040	0.61	0.79	18.80	6.02	6.64	1.70	1.41
FY-H4-1	H4-1	E_2l_3	0.7733	0.136	0.051	0.51	0.73	7.48	1.87	7.55	1.55	1.34
FY-H5-(01)	H5	E_2l_3	0.8047	0.195	0.069	0.41	0.87	10.06	3.55	4.75	1.40	1.02
FY-H5-(02)	H5	E_2l_3	0.7661	0.207	0.029	0.60	0.79	8.04	0.89	9.55	2.50	1.92
FY-H6	H6	E_2l_3	0.8060	0.149	0.105	0.61	0.76	33.88	8.20	3.42	1.17	1.17
FY-H7-(01)	H7	E_2l_3	0.8105	0.291	0.041	0.63	0.85	12.20	0.61	21.56	5.99	4.42
FY-H7-(02)	H7	E_2l_3	0.7610	0.297	0.017	0.62	0.41	10.24	1.20	nd	nd	nd
FY-HD1	Hd1	E_2l_3	0.7864	0.192	0.054	0.64	0.88	26.76	4.69	14.57	3.66	2.60
FY-HD1-1	Hd1-1	E_2l_3	0.8023	0.381	0.045	0.65	0.64	10.48	1.80	12.90	4.14	2.78
FY-HD2	Hd2	E_2l_3	0.8251	0.164	0.058	0.58	0.81	16.74	2.09	5.96	2.29	1.67

a) nd, no data; S, total dibenzothiophenes content; N, total carbazole content; [a]/([a])+[c], benzo[a]carbazole/(benzo[a]carbazole+benzo[c]carbazole); MDR, 4-/1-methyldibenzothiophene; 4,6-/1,4-, 4,6-/1,4-dimethyldibenzothiophene; 2,4-/1,4-, 2,4-/1,4-dimethyldibenzothiophene.

listed in Table 1. Total DBTs content in the Fushan Depression ranges from 0.149—0.381 $mg \cdot g^{-1}$, which is several times higher than that of carbazoles (0.017—0.149 $mg \cdot g^{-1}$) (Table 1). Total DBTs content shows a tendency of positive correlation with total carbazoles contents (Figure 2). Therefore, it is made clear that the

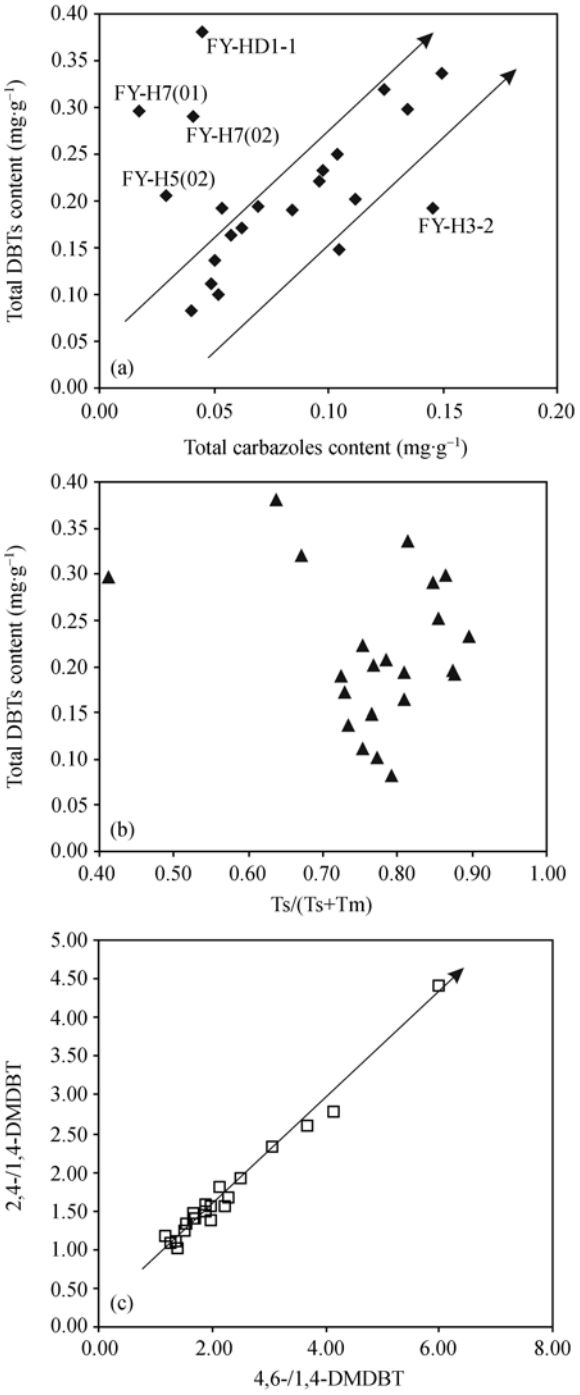

Figure 2 Correlation between (a) total carbazole content and total DBTs content; (b) total content of DBTs and Ts/(Ts+Tm); (c) 2,4-/1,4-DMDBT and 4,6-/1,4-DMDBT.

variations of both total DBTs contents and carbazole compositions are constrained by common factors. Since total carbazole content is a significant parameter to trace oil migration orientation and filling pathway, the new parameter——total DBTs content can yet be regarded as an effective tracer for reservoir filling. Some points, such as wells Hd1-1, H7, H5 and H3-2, deflect away from the positive tendency. In comparison with the samples with similar total contents of DBTs, these samples have relatively lower total carbazoles contents. Their relatively lower total carbazoles content may be caused by the low contents of non-hydrocarbon fraction in these light oils and condensates. As listed in Table 1, these samples mentioned above have a content of non-hydrocarbon fraction as lower as 2.0%, with a minimum of 0.61%. Large errors can be easily caused in the experiment of pyrrolic nitrogen compounds separation, and thus results in inaccurate total carbazoles content.

Some routine tracing parameters from terpanes, such as Ts/(Ts+Tm), which is frequently used in normal oil reservoirs, however, do not show positive correlation with the total DBTs content. It indicates that Ts/(Ts+Tm) is not a significant parameter in light oil or condensate reservoirs of the Fushan Depression. The alkyl DBT parameters, such as 2,4-/1,4-DMDBT, 4,6-/1,4-DMDBT ratios show a fine positive correlation with each other. It indicates that the dibenzothiophene compounds related parameters should be effective tracers for light oil or condensate reservoir filling pathway.

2.3 Tracing result

Situated north of the Hainan Island and south of the Qiongzhou Strait, the Fushan Depression is one of the many Mesozoic-Cenozoic rifting half-grabens in the northern continental shelf of the South China Sea. It is bounded by the Lingao Fault in the northwest, Anding Fault in the south, and Changliu Fault in the southeast. It bears the characteristics of typical half-graben rifting basin. The structural subunits include the northern fault blocks (deep slope), central structural belt and southern slope. The majority of oil and gas discoveries occur in the central structural belt. Four orogenic events occurring during the late Mesozoic to Neogene controlled the tectonic evolution and sedimentary filling of the Beibu Gulf Basin[27,28]. The Shenhu, Zhuqiong, Nanhai and Dongsha orogeny controlled the information of a number of grabens and half-grabens in the Beibu Gulf Basin, the deposition of Changliu (E_1c) and Liushagang For-

mations (E_2l), Weizhou Formation (E_3w), and formations of Neogene. The E_1c and E_3w mainly consist of alluvial and fluvial red pebbled sandstones and mudstones, the E_2l organic-rich mudstones and pebbled sandstones deposited in well-developed lakes.

The discovered oil or gas pools from the Fushan Depression mainly occur in the third (E_2l_3) and first members (E_2l_1) of the Liushagang Formation. The coarse sandstones formed in the braided fan delta front are the main reservoir rocks of E_2l_3 pools. The dark mudstone and shale of the Liushagang Formation are thought to be the source rocks of oil and gas in the Fushan Depression. According to Ding et al.[29], these rocks contain on average 1.51% total organic carbon, with types II and III kerogens. The present burial depth of these rocks exceeds 3000 m, largely within the conventional hydrocarbon generation window[30]. The Huachang oil and gas field that lies in Huachang uplift of the centre structural belt is the greatest field in the Fushan Depression (Figure 3). The hydrocarbons produced in this field include

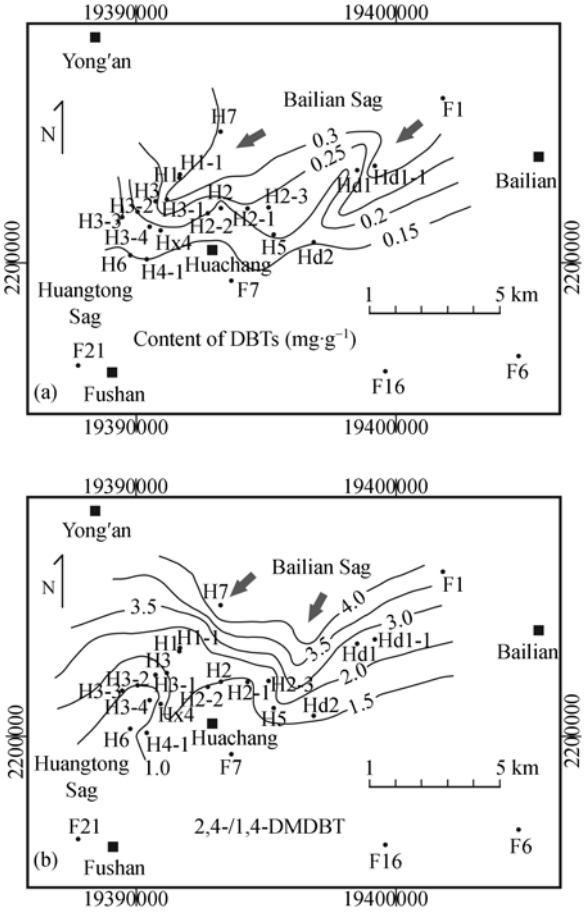

Figure 3 Oil migration orientation and filling pathway traced by (a) total DBTs content contour map; (b) 2,4-/1,4-DBDBT contour map.

natural gas, condensate and light oils. Huangtong and Bailian sags of Eocene Liushagang Formation located to the west and northeast of Huachang uplift, respectively, are thought to be the main hydrocarbon generating sags. Petroleum accumulated in the Huachang uplift may be sourced from the source kitchens of either of these sags or both. Therefore, it is necessary to study the oil migration orientation and filling pathway and then to determine the main source kitchen.

Figure 3(a) illustrates the oil migration and filling pathway indicated by the contour map of total DBTs content. In general, this parameter gradually decreases from the northeast to the southwest along the Huachang uplift. The total DBTs content is about 0.30 $mg \cdot g^{-1}$ near wells H7 and Hd1-1. It decreases to about 0.20 $mg \cdot g^{-1}$ near wells H3-2—H2-1—H5, and the lowest value gets to 0.15 $mg \cdot g^{-1}$ near wells H6~H4-1~Hd2. Total DBTs content in well H3-3 is relatively higher (>0.30 $mg \cdot g^{-1}$) than those of wells H3-2 and H3-1. This well lies in the west part of Huachang uplift and near to the Huangtong Sag. It can be inferred that the oils generated in the Huangtong sag might accumulate in this well. There are two oil filling points in Huachang oil field. One is on the wells H7—H3-1, and oil is charged along the NE orientation to wells H3-2 and Hx4. Another filling point is on well Hd1-1, and oil is charged along the NE orientation to well Hd2.

Figure 3(b) illustrates the oil migration and filling pathway indicated by the contour map of 2,4-/1,4-DMDBT. This ratio also gradually decreases from wells H7—Hd1 to well Hd2, and the lowest value is near wells H6—H4-1. Both DBT parameters indicate that the main source kitchen should be at the Bailian Sag that lies to the northeast of Huachang uplift. The change of oil density, oil to gas ratio and other oil properties have also shown the similar filling process[30]. Although the contour distribution in maps based on different parameters may not be exactly correspondent, the oil migration orientation, filling pathway and filling points are generally consistent with the result indicated by total DBTs content and alkyl DBT parameters.

2.4 Discussion

The basic molecular structure skeleton and properties of DBTs are similar to those of carbazoles. In carbazoles, a hydrogen bond can be formed by the interaction between the hydrogen atom of N—H functional group and

the negative electric atoms (e.g. oxygen atom of organic matter or hydroxyl group of clay minerals). Although there is no similar S—H bond in DBTs, the hydrogen bond can also be formed by interaction between uncoupled lone-pair electron and hydrogen atom in the circumferential medium (e.g. water and organic acid), resulting in molecule adsorption and fractionation during oil migration in reservoir.

In some condensates or severely biodegraded heavy oil reservoir, routine molecular parameters lost their efficacy for the high maturity or destroying by biodegradation, which affect the application of these parameters in filling pathway tracing. Furthermore, large errors may be caused in the pyrrolic nitrogen compound separation experiment for the low content of non-hydrocarbon fraction in condensates or light oils. In condensates from the Fushan Depression, the total DBTs content is much higher than that of carbazoles. The new parameter—total DBTs content and other DBTs related molecular parameters are improved to be effective tracers for oil filling process.

In addition, the DBTs related parameters could be obtained simply by GC-MS of aromatic fraction. In general, the content of aromatic fraction is relatively higher and the analytical error is usually lower. Other aromatic sulfur compounds, such as benzothiophene, benzonaphthothiophenes need to be studied and a set of DBTs related molecular parameters may be established to trace the filling pathway in oil reservoirs.

3 Conclusions

(1) Based on the thermoldynamic stability and hydrogen bond mechanisms, the total dibenzothiophene and alkyldibenzothiophenes (DBTs) content and relative content of isomers are controlled by both maturity and migration fractionation. The total DBTs content can be obtained by elution of quantitative deuterium substituted DBT in GC-MS analysis of aromatic fraction. This parameter shows positive correlation with total carbazole content, which indicates that the total DBTs content is also controlled by the migration fractionation. Therefore, a new parameter——total DBTs content is proposed to be used in the study of oil migration orientation and filling pathway.

(2) For their high maturity, low concentration of steranes and terpanes biomarkers and low content of non-hydrocarbon fraction in condensates and light oils, most frequently used parameters obtained from steranes, terpanes and carbazole nitrogen compounds cannot be effectively applied in the filling pathway study. However, the DBTs exists in a signification concentration, and the total DBTs content can be used as an effective parameter for oil filling pathway tracing.

(3) Owing to their molecular thermodynamic stability, the total DBTs content is applicable for high mature or even over-mature oils.

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