Research paper

Benzo[b]naphthothiophenes and alkyl dibenzothiophenes: Molecular tracers for oil migration distances

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ABSTRACT

The secondary migration of petroleum is one of the most critical geological processes responsible for the accumulation of hydrocarbons in a sedimentary basin. Pyrrolic nitrogen compounds such as carbazoles and benzocarbazoles are thought to be practical molecular indicators for estimating relative migration distances of oil. In light oils or condensates, however, considerable analytical errors are usually caused by low concentrations of NSO-compounds. Here we show that polycyclic sulfur aromatic hydrocarbons such as dibenzothiophene, $C_1 \sim C_3$ alkylated dibenzothiophenes and benzo[b]naphthothiophenes, which are present in relatively higher concentrations than the pyrrolic nitrogen compounds, exhibit changes in both absolute and relative concentrations that correlate with migration distances. The polycyclic sulfur aromatic hydrocarbons related parameters — benzo[b]naphtho[2,1-d]thiophene/{benzo[b]naphtho[2,1-d]thiophene + benzo[b]naphtho[1,2-d]thiophene} (abbreviated as [2,1]BNT/([2,1]BNT+[1,2]BNT) and the concentration of total dibenzothiophenes plus benzo[b]naphthothiophenes — are proposed by this paper to trace the oil migration distances.

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1. Introduction

Reconstruction of oil migration directions, pathways, and distances is vital to define potential source kitchens and predict commercial "satellite accumulations" in a sedimentary basin (England et al., 1987). Since seismic or other remote-sensing surveys cannot provide explicit information about secondary oil migration, some biomarkers have been successfully applied to define regional petroleum migration directions and pathways (Horstad et al., 1995; Peters et al., 2005). Pyrrolic nitrogen compounds have been proved to be practical molecular indicators for tracing oil migration directions, pathways, and distances (Larter et al., 1996; Li et al., 1998, 1999). In condensates or light oil reservoirs, however, the application of these compounds has encountered some limitations (Li et al., 2008a). Furthermore, other factors such as source organic matter input, depositional environment, biodegradation, and thermal maturity may have a significant impact on the distribution of pyrrolic nitrogen compounds in sedimentary basins (Li et al., 1999; Silliman et al., 2002; Zhang et al., 2013).

Condensates and light oils are generally characterized by relatively high maturity, low density, and low asphaltene and NSO-hydrocarbon content. Higher-molecular-weight components, including biomarkers, occur in low concentrations or are absent in many condensates (Peters et al., 2005). This presents analytical challenges due to their low signal-to-noise ratios in gas chromatography—mass spectrometry (GC—MS) analyses and prevents the application of many frequently used geochemical parameters (Peters et al., 2005). The low concentration of NSO-compounds in condensates and light oils will unavoidably lead to relatively large analytical errors during the separation and quantification of the total concentrations of pyrrolic nitrogen compounds (Li et al., 2008a). In addition, light oils and condensates are chemically composed mainly of low molecular weight hydrocarbons, which readily volatilize during the analysis. The application of biomarkers and pyrrolic nitrogen compounds for migration studies is thus inappropriate for the light oil or condensate reservoirs (Li et al., 2008a).

One of the main forms of organic sulfur in crude oil is thiophene-class compounds where sulfur is bound to polycyclic aromatic hydrocarbons including alkylated benzothiophenes (BTs), dibenzothiophene (DBT) and its, $C_1 \sim C_3$ alkyl derivatives (DBTs). These compounds can be detected in the aromatic fraction of crude oil and sediment extracts by routine GC—MS analysis. DBT and two

methyldibenzothiophene isomers (MDBTs) in crude oils were detected in the 1980s (Hughes, 1984; Connan et al., 1986). The presence of dimethyldibenzothiophene isomers (DMDBTs) and trimethyldibenzothiophenes (TMDBTs) in crude oils were subsequently confirmed in the 1990s (Budzinski et al., 1991; Chakhmakhchev et al., 1997; Mössner et al., 1999). Due to the diverse molecular thermodynamic stability of alkyl substitution at different positions of the DBT carbon skeleton (Budzinski et al., 1991; Richard, 2001; Szczerba and Rospondek, 2010), DBT-related molecular markers were used by most researchers mainly as maturity indicators (Radke, 1988; Radke et al., 1991; Budzinski et al., 1991; Bao et al., 1996; Chakhmakhchev et al., 1997; Santamaría-Orozco et al., 1998; Kruge, 2000; Li et al., 2013a, 2013b). In addition, the DBT abundance is also dependent on source rock type and sedimentary environment (Hughes, 1984; Connan et al., 1986; Budzinski et al., 1991; Hughes et al., 1995; Chakhmakhchev et al., 1997; Santamaría-Orozco et al., 1998; Huang and Pearson, 1999; Li, 2000; Hwang et al., 2002; Yang et al., 2005). The basic molecular skeleton of DBTs is similar to that of carbazoles, but the five-membered ring in DBTs is a sulfur-containing thiophenic ring, instead of a nitrogen-containing pyrrolic ring.

The molecular fractionation produced during oil migration may be mainly controlled by geochromatography, similar to the normal phase chromatographic process, of which liquid−solid chromatography is the most important one (Krooss et al., 1991). Adsorption is considered by most researchers to be the predominant mechanism during the geochromatographic process. The absorption characteristics of hydrocarbons in migrated oils are mainly controlled by the hydrogen bond and dipole−dipole interaction. Oil/water partitioning is also another possible mechanism for oil migration fractionation (van Duin and Larter, 2001; Yang et al., 2005).

In carbazoles, a hydrogen bond can be formed by the interaction between the N−H functional group and the atoms with stronger electronegativity, such as the oxygen atom (with an electronegativity value of 3.5) in organic matter or a film of hydroxyl groups on clay mineral surfaces. This process can result in molecular adsorption and fractionation of carbazole isomers during oil migration and thus, carbazoles can be used to determine the pathways and distances of oil migration (Li et al., 1995; Larter et al., 1996; Wang et al., 2004a).

There are unshared pairs of electrons in the outer shell orbital of a sulfur atom. Hydrogen bonds can also be formed between sulfur in the thiophene ring and the hydrogen atoms of organic matter in carrier beds (Wang et al., 2004b; Li et al., 2008a). The main difference is that the hydrogen atom in carbazoles is an electron acceptor, whereas the sulfur atom in the DBTs is an electron donor. They can both form a hydrogen bond with clay minerals which can provide an electron donor (oxygen atom), or organic matter which can provide an electron acceptor (hydrogen atom).

In this study, we have further exploited other sulfur heterocyclic aromatic compounds—three isomers of benzo[b]naphthothiophenes to investigate their migration fractionation effects. Some novel geochemical parameters such as benzo[b]naphtho[2,1-d]thiophene/{benzo[b]naphtho[2,1-d]thiophene + benzo[b]naphtho[1,2-d]thiophene} have been proposed to indicate migration distances.

2. Samples and geological settings

A total of 83 oils and condensates were collected from the Tahe oil field in the Tarim Basin (Table 1), Northwest China and the Beibuwan Basin (Table 2), South China Sea. Oils in the Tahe oil field were derived from typical marine-carbonate source rocks (Zhang

and Huang, 2005; Wang et al., 2008; Li et al., 2012b), whereas light oils and condensates in the Fushan Depression, Beibuwan Basin are of terrigenous origin (Li et al., 2008b).

The Tarim Basin, situated in the south of Xinjiang Uygur Autonomous Region, northwest China is a Paleozoic cratonic basin, overlain in the north and south by Mesozoic−Cenozoic foreland depressions (Fig. 1) (Li et al., 1996). Detailed geological features of the Tarim Basin have been studied at length by numerous authors (e.g., Li et al., 1996; Jia and Wei, 2002; Zhang and Huang, 2005).

The stratigraphy of the Tarim Basin consists of several marine, continental and transitional sequences. The Paleozoic strata were deposited almost entirely in marine settings (Li et al., 1996; Jia and Wei, 2002). The ~3 km of Cambrian−Lower Ordovician strata consists of shallow marine to lagoonal carbonates, whereas the Middle−Upper Ordovician was deposited during a marine transgression event. Following the deposition of the Silurian and Devonian fine-grained sandstones and red beds, ~1 km of upper Paleozoic marine and continental transitional sediments were deposited. After a major Late Permian hiatus, renewed subsidence led to the deposition of as much as 6 km of Mesozoic−Cenozoic fluvio-lacustrine sediments (Li et al., 2010).

The source rocks occur mainly in the lower Paleozoic sequence, including the currently overmature Cambrian to Lower Ordovician and the mature Middle−Upper Ordovician at peak oil generation (Xiao et al., 1996; Hanson et al., 2000; Zhang et al., 2000). Oil and gas accumulations are in the Cambrian-Ordovician carbonate reservoirs and in the overlying Carboniferous, Triassic, Jurassic and Cretaceous sandstones, as a result of lateral and vertical migration (Graham et al., 1990; Jia and Wei, 2002; Wang et al., 2008). All the oil samples in this study were collected from the Ordovician carbonate reservoirs.

The majority of the discovered oils in the Tahe oil field, Tarim Basin are derived from the Middle−Upper Ordovician carbonate source rocks located to the south of the Tabei Uplift (Zhang et al., 2000; Wang et al., 2004b, 2008). The source kitchen may lie to the south side of the oil field, at the Shuntuoguole Lower Uplift between the Awati and Manjiaer depression (Wang et al., 2008).

Located in the south of the Qiongzhou Strait and north of Hainan Island, the Fushan Depression is one of the many Mesozoic−Cenozoic rifting half- grabens in the northern continental shelf of the South China Sea (Fig. 2). This NE-SW trending depression, forming the southeastern part of the Beibuwan Basin (Li et al., 2008b), is filled with as much as 9000 m of Cenozoic sediments in an area of about 3000 km^2 (Li et al., 2008b).

Known petroleum reservoirs in the Fushan Depression include pay zones in the E_2l_3, E_2l_2 and E_2l_1 members of the Eocene Liushagang Formation. The light oils and condensates in the Fushan Depression mainly originated from the source rocks of the Eocene Liushagang Formation in the Bailian Sag, which is located to the northeast of the oil fields (Li et al., 2008b, 2009).

In order to investigate the effects of maturity on the concentrations of DBT compounds, a set of source rock samples from the Well SG1 in the Western Depression, Bohai Bay Basin, NE China were collected. All rocks were sampled from the third member of Eocene Shahejie Formation, which is the main source bed for the discovered oil accumulations in the Western Depression (Hu et al., 2005).

3. Experiments and methods

3.1. Rock extract

Rock−Eval analyses were carried out on approximately 50 mg of crushed source rocks ($n = 21$), using a Rock−Eval 6 instrument in

Table 1
Selected parameters of the crude oil samples from the Tahe oil field Tarim Basin used in this study.

Sample Code	Gross composition (%)			Pr/Ph	C29 sterane		Triterpane					MPI		Naphthalene	
	SAT	ARO	NSO + ASPH		S/(S + R)	ββ/(ββ+αα)	Ts/(Ts + Tm)	22S/(22S + 22R)	C30 Dia/C30 H	C29/C30	C35/C34	1	2	TMNr	TeMNr
Ad5	28.34	25.51	46.15	0.74	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.70	0.85	0.56	0.56
Ad5-02	23.38	27.65	48.97	0.85	0.50	0.51	0.28	0.54	0.05	1.21	1.06	0.72	0.90	0.51	0.55
Ad6	28.89	25.46	45.65	0.63	0.48	0.53	0.27	0.54	0.09	1.44	1.06	0.68	0.83	0.50	0.53
Ad7	34.67	26.29	39.04	0.66	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.68	0.85	0.54	0.59
Ad8	25.06	23.19	51.75	0.83	0.45	0.53	0.30	0.55	0.10	1.23	0.90	0.68	0.81	0.47	0.44
Ad9	25.68	27.40	46.92	0.66	0.47	0.54	0.30	0.55	0.10	1.19	0.90	0.74	0.92	0.50	0.57
Ad11	27.28	24.35	48.37	0.48	0.49	0.56	0.27	0.54	0.10	1.23	0.87	0.71	0.91	0.49	0.56
Ad13	24.72	21.27	54.01	0.64	0.51	0.50	0.29	0.54	0.13	1.35	0.95	0.76	0.95	0.43	0.55
Ad15	26.01	21.96	52.03	0.76	0.50	0.53	0.23	0.53	0.11	1.09	0.83	0.69	0.84	0.47	0.60
Ad16	20.96	17.14	61.90	1.04	0.47	0.53	0.27	0.50	0.12	0.77	0.96	0.69	0.82	0.45	0.53
Tk1004	42.92	25.00	32.08	0.72	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.61	0.75	0.64	0.68
Tk1007CH	29.96	30.9	39.14	0.68	0.48	0.54	0.25	0.55	0.05	1.04	0.98	0.66	0.78	0.55	0.65
Tk1012-1	31.18	29.53	39.29	0.61	0.51	0.52	0.25	0.53	0.04	1.19	1,12	0.63	0.77	0.51	0.52
Tk1012-2	35.80	34.78	29.42	0.69	0.50	0.53	0.27	0.51	0.04	1.33	0.98	0.76	0.80	0.53	0.60
Tk1013	48.04	22.27	29.69	0.71	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.68	0.81	0.64	0.66
Tk1017	35.04	29.92	35.04	0.57	0.55	0.54	0.23	0.56	0.04	1.22	1.22	0.66	0.79	0.52	0.57
Tk1017-2	36.70	28.24	35.06	0.56	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.63	0.73	0.51	0.56
Tk1020	27.40	24.91	47.69	0.59	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.68	0.77	0.61	0.58
Tk1024	27.67	44.52	27.81	0.80	0.51	0.54	0.33	0.53	0.05	0.90	0.72	0.65	0.72	0.57	0.62
Tk1026	28.99	25.36	45.65	0.65	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.71	0.85	0.54	0.58
Tk1027CH	35.54	28.49	35.97	0.62	0.51	0.53	0.23	0.54	0.04	1.14	1.09	0.67	0.74	0.53	0.54
Tk1029	21.26	25.58	53.16	0.75	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.75	0.94	0.46	0.52
Tk1032	22.90	22.02	55.08	0.64	0.50	0.56	0.25	0.55	0.06	1.00	1.12	0.65	0.86	0.48	0.53
Tk1034	31.90	30.71	37.39	0.74	0.47	0.56	0.29	0.53	0.04	1.02	1.09	0.66	0.73	0.59	0.57
Tk1035	29.13	46.30	24.57	0.81	0.50	0.54	0.35	0.54	0.06	0.95	0.84	0.60	0.70	0.55	0.61
Tk1037	22.77	17.82	59.41	0.82	0.48	0.54	0.32	0.54	0.12	1.38	1.06	0.72	0.87	0.50	0.57
Tk1039	27.61	23.46	48.93	0.64	0.51	0.53	0.23	0.53	0.06	1.24	1.33	0.66	0.83	0.50	0.52
Tk1044	30.43	19.44	50.13	0.55	0.49	0.58	0.24	0.55	0.05	1.09	1.19	0.69	0.83	0.47	0.47
Tk1110X	55.65	24.78	19.57	0.69	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.65	0.76	0.62	0.66
Tk1201	26.92	29.76	43.32	0.77	0.51	0.56	0.31	0.55	0.08	1.26	1.02	0.71	0.87	0.48	0.59
Tk1212	26.39	25.09	48.52	0.61	0.47	0.54	0.30	0.55	0.06	1.04	0.92	0.64	0.85	0.54	0.56
Tk1213	28.96	29.07	41.97	0.63	0.48	0.56	0.29	0.52	0.12	1.40	1.02	0.75	0.94	0.51	0.58
Tk1215-2	23.18	21.14	55.68	0.54	0.50	0.55	0.27	0.56	0.12	1.35	1.26	0.72	0.91	0.50	0.55
Tk1221	27.27	18.09	54.64	0.58	0.50	0.57	0.26	0.55	0.06	1.24	1.29	0.76	0.80	0.55	0.49
S94-1	24.81	16.04	59.15	0.71	0.47	0.51	0.26	0.52	0.09	1.24	1.21	0.39	0.44	0.48	0.54
Tp7-2	57.37	25.36	17.27	0.81	0.47	0.58	0.36	0.54	0.05	0.97	0.86	0.61	0.69	0.57	0.69
Tp9	65.50	21.83	12.67	0.86	0.48	0.56	0.40	0.50	0.07	0.94	0.84	0.63	0.74	0.65	0.81
Tp10X	74.81	16.39	8.80	0.92	0.49	0.48	0.46	0.49	0.08	1.06	0.90	0.63	0.68	0.72	0.86
Tp12CX	73.50	17.45	9.05	0.86	0.47	0.53	0.50	0.54	0.06	0.85	0.70	0.65	0.75	0.67	0.77

Note : SAT, ARO and NSO + ASPH : percentage of saturated, aromatic, NSO and asphaletene fractions of oils. Pr/Ph : pristane/phytane; S/(S + R) : C29 sterane 20S/(20S + 20R); ββ/(ββ+αα): C29 sterane ββ/(ββ+αα); Ts/(Ts + Tm) : 18α-22,29,30-trinorhopane/(18α-22,29,30-trinorhopane+17α-22,29,30-trinorhopane); 22S/(22S + 22R): C30 hopane 22S/(22S + 22R); C30 Dia/C30 H : C30 diahopane/C30 hopane; C29/C30: C29 hopane/C30 hopane; C35/C34: C35 homohopane/C30 hopane; MPI-1: 1.5 × (2-MP+3-MP)/(Phenanthrene+1-MP+9-MP), MP: methylphenanthene; MPI-2 : 3 × (2-MP)/(Phenanthrene+1-MP+9-MP); TMNr: 1,3,7-TMN/(1,3,7-TMN +1,2,5-TMN), TMN: trimethylnaphthalene; TeMNr: 1,3,6,7-TeMN/(1,3,6,7-TeMN+1,2,5,6-TeMN+1,2,3,5-TeMN), TeMN: tertramethylnaphthalene.

which the oxidation oven was programmed to ramp temperature between 400 and 800 °C. Twenty-one rock samples were extracted by using a Soxhlet extractor with about 500 ml of dichloromethane and methanol (83:17 v/v).

All oil samples and rock extracts were treated with a standard analytical procedure. Oils were deasphaltened using *n*-hexane and then fractionated by liquid chromatography using silica gel/ alumina columns into saturated and aromatic hydrocarbon fractions using *n*-hexane and dichloromethane (50:50 v:v) and dichloromethane as eluents, respectively.

The pyrrolic nitrogen fraction was separated by using a "two-stage isolation method" (Li et al., 1999a,b; Bennett and Olsen, 2007). Deasphaltened oil was fractionated by liquid chromatography using alumina columns (7 g) into saturated, non-hydrocarbon and aromatic hydrocarbon fractions using petroleum ether (50 ml), chloroform and methanol (70 ml. 98:2 v:v), and toluene (50 ml) as eluents, respectively. The pyrrolic nitrogen fractions can be separated from the non-hydrocarbon fraction by using silica-gel liquid chromatography columns (2.5 g) using toluene and *n*-hexane (60 ml, 50:50 v:v) as eluant.

3.2. Gas chromatography–Mass spectrometry analysis

Gas Chromatography–Mass Spectrometric (GC–MS) analysis of the saturated hydrocarbon fractions of oils and extracts was performed by using an Agilent 5975i mass spectrometer, coupled with an HP 6890 GC equipped with an HP-5MS column (60 m × 0.25 mm) with a 0.25 μm coating. Helium was used as the carrier gas. The GC oven temperature was initially set to 50 °C, and programmed to 120 °C at 20 °C/min, then to 310 °C at 3 °C/min with a final hold of 25 min. The mass spectrometer was operated in full-scan mode. Electron impact ionization was employed (70 eV).

GC/MS analysis on the pyrrolic nitrogen fractions was performed by using an Agilent 5975i mass spectrometer combined with a gas chromatograph equipped with a 60-m long fused-silica capillary column (HP-5MS, 0.25 mm i.d., 0.25-m film thickness). The GC oven was initially set to 80 °C for 1 min, followed by a ramp up to 150 °C at 15 °C/min and then to 290 °C at 5 °C/min with a final hold of 20 min. The mass spectrometer was operated in selective-ion monitoring (SIM) mode with electron impact ionization of 70 eV. The absolute and relative concentrations of carbazoles and

Table 2
Summary of carbazoles, C_1 to C_3 alkylcarbazoles, benzocarbazoles, dibenzothiophene, C_1–C_3 alkyldibenzothiophenes and benzonaphthothiophenes of oils from Beibuwan Basin, South China Sea.

Sample code	Concentration of CAs and BCAs (μg/g oil)						Concentration of DBTs and BNTs (μg/g oil)						[a]/([a]+[c])	[[2,1]BNT]/ ([[2,1]BNT]+[[1,2]BNT])	Relative migration distance (km)
	CA	MCA	DMCA	TMCA	BCA	N	DBT	MDBT	DMDBT	TMDBT	BNT	S			
Ad5	4.27	16.23	46.10	23.97	3.61	94.18	52.80	139.67	267.41	199.00	37.69	696.57	0.53	0.77	35
Ad5-02	3.89	16.81	51.36	26.64	3.72	102.42	56.76	149.78	278.63	195.74	26.13	707.04	0.51	0.74	35
Ad6	4.40	17.45	49.85	25.40	3.45	100.54	45.07	123.18	223.73	150.30	24.87	567.16	0.54	0.74	36
Ad7	4.83	20.85	62.94	33.44	3.09	125.14	64.86	176.18	304.99	215.97	39.81	801.81	0.59	0.82	37
Ad8	3.73	9.93	24.97	11.42	2.38	52.42	26.56	66.66	102.86	51.14	14.21	261.43	0.52	0.73	51
Ad9	4.80	21.26	59.08	32.26	3.96	121.36	57.43	154.08	258.91	177.18	24.26	671.86	0.57	0.77	39
Ad11	4.05	18.56	52.07	27.52	2.65	104.86	51.16	135.49	217.41	126.12	22.92	553.09	0.54	0.79	39
Ad13	3.85	13.96	34.35	16.01	2.69	70.86	24.23	67.26	108.71	58.17	12.59	270.95	0.53	0.71	41
Ad15	4.61	19.14	52.19	24.51	3.00	103.46	73.81	189.95	288.47	123.65	18.10	693.99	0.58	0.74	47
Ad16	2.79	12.47	39.85	19.61	3.23	77.95	57.45	153.59	202.43	81.44	15.36	510.28	0.57	0.78	44
Tk1004	3.13	11.67	37.75	21.09	3.47	77.11	58.59	191.43	338.41	209.10	33.02	830.55	0.59	0.84	29
Tk1007CH	2.80	12.11	39.74	25.76	4.17	84.58	102.15	331.03	601.31	321.54	32.83	1388.86	0.57	0.76	25
Tk1012-1	3.88	18.31	56.67	33.11	3.60	115.56	110.82	320.72	619.00	382.61	41.59	1474.74	0.54	0.79	27
Tk1012-2	4.32	21.00	66.94	36.76	3.56	132.58	117.16	342.14	650.62	305.95	34.41	1450.28	0.58	0.76	27
Tk1013	5.08	25.22	81.52	41.98	4.65	158.45	73.12	244.69	424.60	329.80	27.55	1099.75	0.63	0.79	30
Tk1017	4.39	17.22	51.37	26.77	5.10	104.87	54.00	157.90	311.10	200.78	46.02	769.80	0.59	0.78	29
Tk1017-2	4.03	17.10	52.44	29.88	5.05	108.51	118.54	346.08	630.88	375.54	56.18	1527.23	0.55	0.81	29
Tk1020	2.13	5.89	14.58	7.21	1.85	31.65	15.56	41.75	86.08	57.14	14.16	214.69	0.54	0.72	36
Tk1024	4.89	21.55	56.64	33.40	4.48	120.96	137.22	456.89	791.90	505.75	78.00	1969.77	0.62	0.84	18
Tk1026	4.70	15.02	39.95	19.73	3.07	82.47	36.15	90.62	180.89	142.20	29.88	479.75	0.61	0.79	31
Tk1027CH	3.87	15.95	47.96	26.33	4.15	98.27	100.43	299.07	513.68	336.40	45.01	1294.58	0.53	0.80	28
Tk1029	3.83	13.59	34.64	16.41	3.34	71.82	21.66	59.53	109.65	79.42	19.92	290.18	0.57	0.76	36
Tk1032	2.76	11.61	32.16	17.47	1.92	65.92	50.44	131.78	209.39	141.26	31.91	564.78	0.53	0.76	34
Tk1034	3.17	6.76	13.51	7.33	1.74	32.50	35.01	113.79	203.84	141.61	22.39	516.64	0.52	0.78	34
Tk1035	5.66	22.78	59.29	30.44	4.28	150.00	154.03	512.56	897.85	568.78	89.48	2222.70	0.61	0.83	15
Tk1037	2.13	8.91	25.31	13.78	1.86	51.99	45.40	135.81	231.69	145.25	16.33	574.49	0.55	0.74	33
Tk1039	4.15	20.24	67.07	38.40	2.95	132.80	103.08	275.65	500.39	404.11	37.20	1320.43	0.56	0.80	31
Tk1044	1.61	5.94	16.70	8.66	1.41	34.32	35.51	98.74	168.38	104.90	16.20	423.73	0.48	0.72	35
Tk1110X	2.09	8.73	30.79	19.15	2.37	63.12	50.13	179.97	319.76	195.80	29.85	775.51	0.64	0.84	34
Tk1201	3.16	17.49	57.82	31.89	2.14	112.50	142.44	362.18	566.80	338.82	35.88	1446.12	0.55	0.75	35
Tk1212	3.85	17.79	53.64	26.06	2.66	103.99	98.98	254.49	384.31	283.27	28.41	1049.47	0.55	0.77	39
Tk1213	3.43	17.66	57.48	29.24	1.82	109.62	105.25	272.90	444.83	237.99	27.13	1088.10	0.54	0.76	40
Tk1215-2	3.47	16.45	48.96	22.47	2.78	94.13	65.18	163.88	273.29	155.46	21.67	679.49	0.56	0.74	41
Tk1221	2.30	8.25	21.47	9.32	0.83	42.16	22.98	65.27	126.88	77.07	13.75	305.96	0.46	0.66	50
S94-1	4.90	13.46	33.25	15.60	5.76	72.98	45.52	111.67	174.18	112.94	39.78	484.09	0.54	0.78	43
Tp7-2	3.33	18.87	62.48	37.04	3.52	125.25	176.72	535.24	777.66	450.71	46.00	1986.33	0.66	0.89	13
Tp9	5.54	31.62	103.31	56.87	6.08	203.42	155.45	572.00	845.93	436.41	33.80	2043.59	0.65	0.86	13
Tp10X	7.40	37.71	103.93	47.27	5.08	201.38	156.62	523.91	724.86	408.64	34.03	1848.05	0.67	0.87	6
Tp12CX	5.05	26.34	75.58	37.29	5.29	149.54	160.85	546.57	900.96	469.40	38.69	2116.48	0.64	0.87	1

N Note: Definition of parameters. CA, MCA, DMCA, TMCA, BCA: absolute concentrations of carbazole, methylcarbazoles, dimethylcarbazoles, trimethylcarbazoles and benzocarbazoles in oils (μg/g oil), N: the total concentrations of CA, MCA, DMCA, TMCA and BCA; DBT, MDBT, DMDBT, TMDBT, and BNT: the absolute concentrations of dibenzothiophene, methyldibenzothiophenes, dimethyldibenzothiophenes, trimethyldibenzothiophenes, and benzo[b]naphthothiophenes. S: the total concentrations of DBT, MDBT, DMDBT, TMDBT, and BNT. [a]/([a]+[c]): The ratio of benzo[a]carbazole/(benzo[a]carbazole + benzo[c]carbazole); [2,1]BNT/([2,1]BNT+[1,2]BNT): the ratio of benzo[b] naptho[2,1-d]thiophene/(benzo[b]naphtha[2,1-d]thiophene + benzo[b]naphtha[1,2-d]thiophene).

benzocarbazoles were obtained following the same procedure described by Li et al. (1995) and using 9-phenylcarbazole as an internal standard.

The GC–MS analysis of the aromatic hydrocarbon fractions was performed on an Agilent 5975i mass spectrometer system coupled with an HP-5MS fused-silica capillary column (60 m × 0.25 mm i.d.) with a 0.25 μm coat. The GC operating conditions are as follows: (1) the GC oven temperature was set to an initial 80 °C for 1 min, programmed to increase to 310 °C at 3 °C/min, and then kept isothermal for 16 min. Helium was used as a carrier gas. The injector temperature was set to 300 °C. The MS was run by electron impact ionization (EI) at 70 eV, in full-scan mode with a scanning range of 50–600 a.m.u./s.

3.3. Qualitative and quantitative analysis

In comparison with the relative retention time and retention indices on m/z 184, 198, 212, and 226 mass chromatograms published by previous authors (Budzinski et al., 1991; Chakhmakhchev et al., 1997; Mössner et al., 1999; Schade and Andersson, 2006; Li

et al., 2012a, 2013a, 2013b), dibenzothiophene (DBT), methyldibenzothiophene (MDBTs), dimethyldibenzothiophene (DMDBTs), and trimethyldibenzothiophenes (TMDBTs) were confidently assigned and confirmed in the samples analyzed (Fig. 3). DBT with eight-substituted deuterium atoms ($C_{12}D_8S$) was added in the samples as an internal standard during GC–MS analysis. The peak of $C_{12}D_8S$ can be identified on the m/z 192 mass chromatograms, which elutes just before the methylphenanthrene peaks (Fig. 3). By correlation with the peak area of $C_{12}D_8S$, the absolute concentrations of DBT and alkyl DBTs were determined. By co-injection with an internal standard phenyl carbazole, the absolute concentrations of carbazoles and benzocarbazoles can also be determined by a similar approach.

Three isomers of benzo[b]naphtha[2,1-d]thiophene (abbreviated as [2,1]BNT), benzo[b]naphtho[1,2-d]thiophene ([1,2]BNT) and benzo[b]naphtho[2,3-d]thiophene ([2,3] BNT) were detected in oils by using the internal standard compounds (purity > 99.0%, Laboratory of Dr. Ehrenstorfer, Augsburg, Germany) in the GC–MS analysis of the aromatic fraction of oils (Fig. 4) and by comparing with mass chromatograms published in literature.
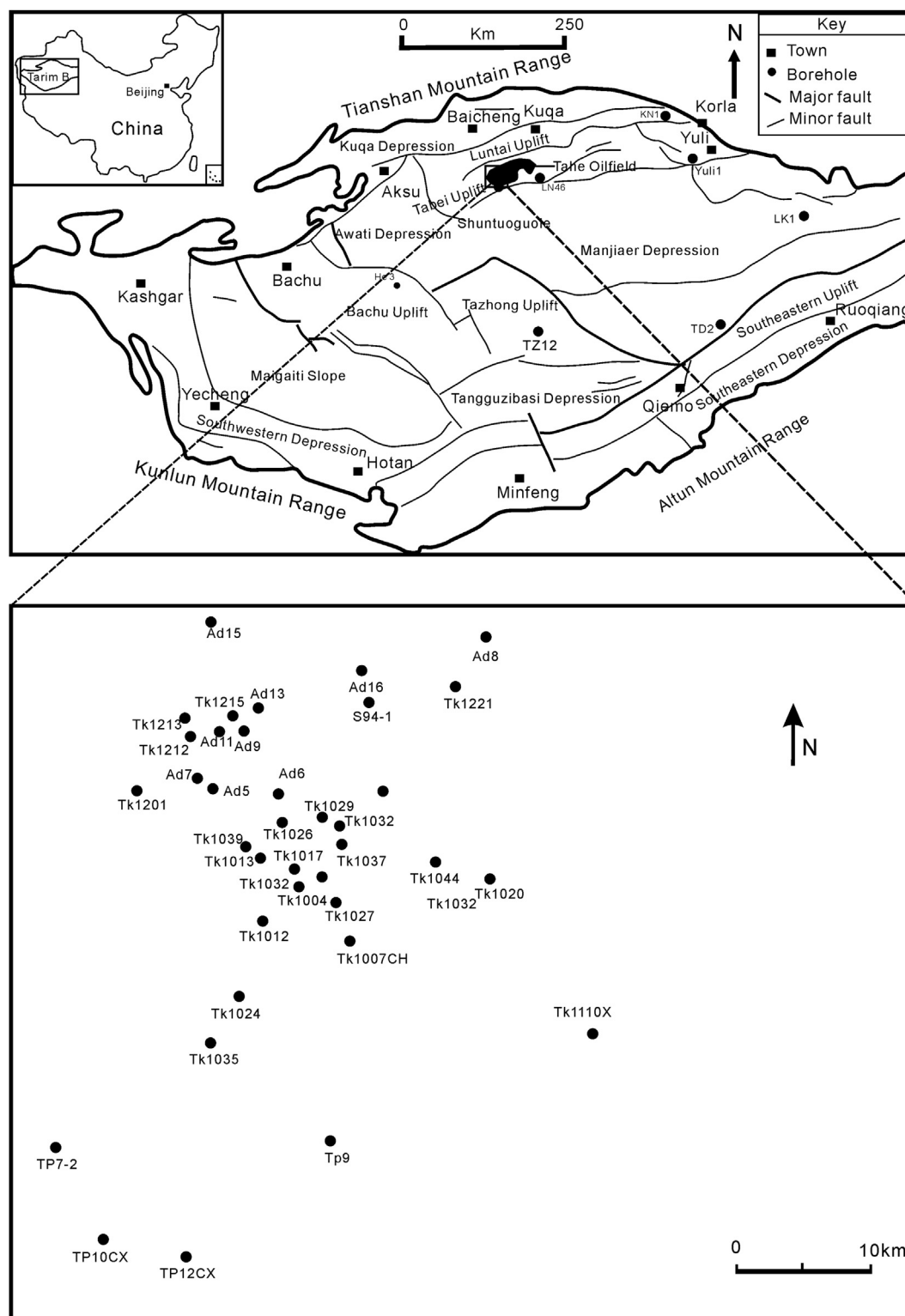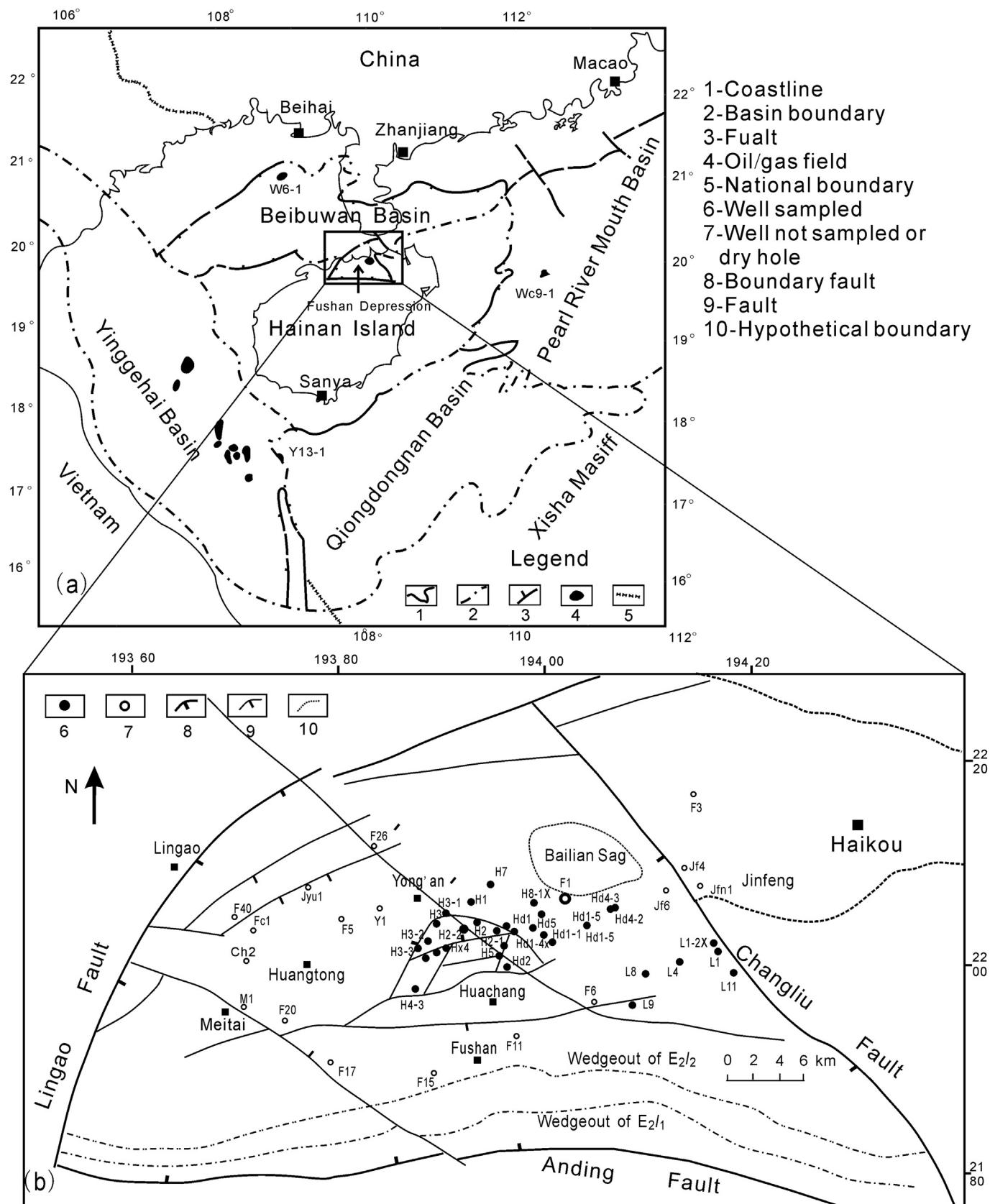
Figure 1. Map showing well locations of the Tahe oil field and major tectonic terranes in the Tarim Basin, China (After Wang et al., 2008).

4. Results and discussion

4.1. Molecular structure and chemical properties

The electronegativity value of sulfur (2.6) is less than that of nitrogen (3.04), and exhibits relatively lower inductive effects. The conjugative effect of the sulfur atom in the thiophenic ring, however, is much less than that of the nitrogen atom in the pyrrolic ring due to the conjugation of the five-membered aromatic ring carbons with 3p electrons in the sulfur atom compared to 2p electrons in the nitrogen atom. The dipole moment of the dibenzothiophene is 0.84 Debye (Vysotskill et al., 1981), which is about half of that in the

Figure 2. Map showing well location of the Fushan Depression, Beibuwan Basin, South China Sea (After Li et al., 2009).
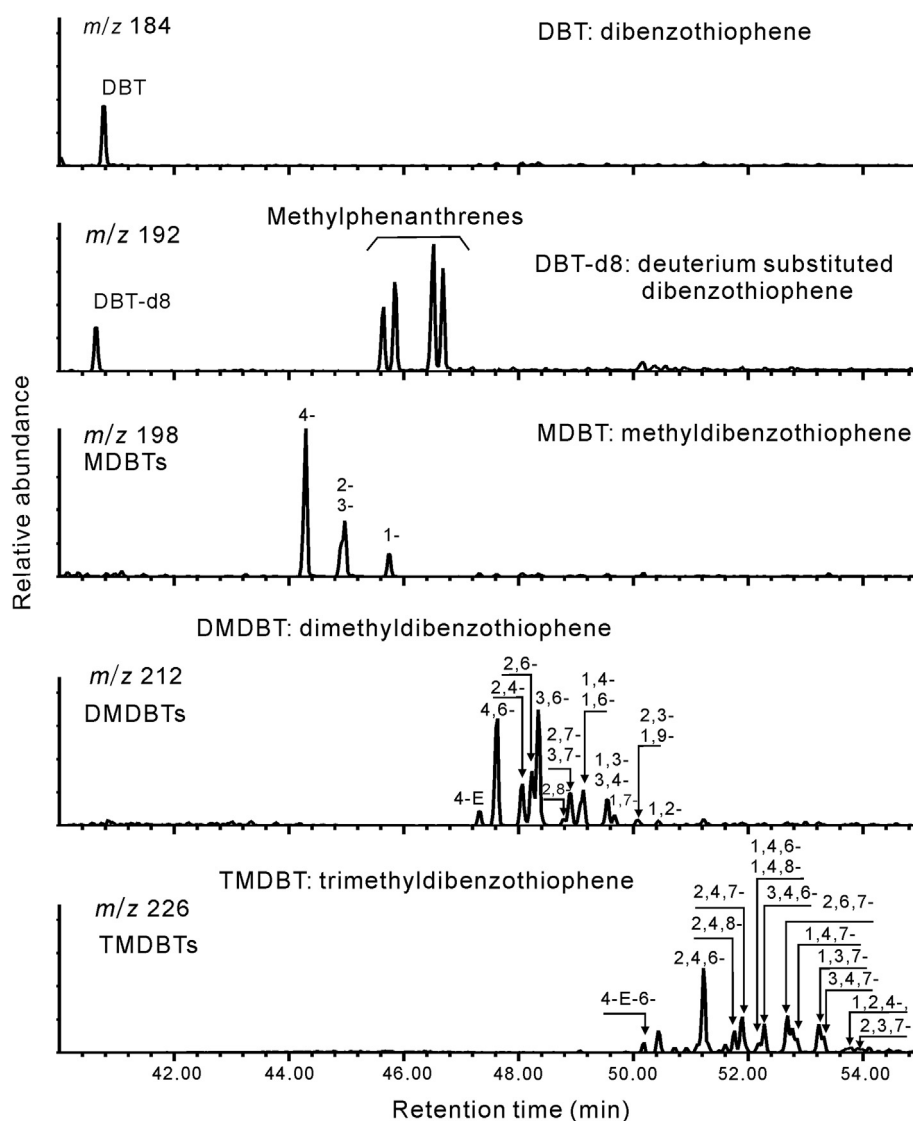
Figure 3. Example mass chromatograms showing peaks of dibenzothiophene, alkyldibenzothiophenes, and internal standard (deuterium substituted dibenzothiophene ($C_{12}D_8S$). The isomers of methyl-, dimethyl- and trimethyl-dibenzothiophenes are identified on m/z 198, 212 and 226 mass chromatograms referencing to the retention indices and relative retention time and published in the literature (e.g., Budzinski et al., 1991; Chakhmakhchev et al., 1997; Mössner et al., 1999; Schade and Andersson, 2006). Numbers on peaks indicate the methyl substitution pattern on DBT, DMDBTs and TMDBTs. By correlation with the peak area of $C_{12}D_8S$, the absolute concentration of DBT, alkyl DBTs can be determined.

carbazoles (1.7 Debye) (Shimamori and Sato, 1994). Dibenzothiophene is a polar heterocyclic aromatic compound, which can interact with polar compounds in the carrier beds during oil migration. Both the hydrogen bond and the dipole–dipole interaction mechanism theoretically would cause a fractionation effect of DBTs during the oil migration process. Moreover, due to their relatively high aqueous solubility, aromatic and sulfur-bearing compounds, especially dibenzothiophenes may be fractionated by a liquid–liquid chromatographic effect similar to the water-washing process (Lafargue and Barker, 1988).

In spite of their relatively low concentrations in oils compared to DBTs, three isomers of benzo[b]naphtha[2,1-d]thiophene, benzo[b] naphtho[1,2-d]thiophene, and benzo[b]naphtho[2,3-d]thiophene (abbreviated as [2,1]BNT, [1,2]BNT, and [2,3]BNT, respectively; see Misra and Amin, 1990) were detected in this study by using internal standards in the GC−MS analysis of the aromatic fraction of oils (Fig. 4) and by comparison with mass chromatograms published in the literature (Karcher et al., 1985). The former two isomers which have similar structures to that of benzo[a]carbazole and benzo[c]

carbazole (Fig. 5) exist in significant quantities in oils. Like benzo[b] carbazole, benzo[b]naphtho[2,3-d]thiophene is usually present in very low concentrations and is generally undetectable by routine full-scan GC−MS analyses (Figs. 4 and 5). The gas chromatographic retention behavior of benzo[b]naphthothiophenes and the alkyl-substitute derivatives on different stationary phases were previously reported (Mössner et al., 1999; Schade and Andersson, 2006; Li et al., 2012a); however, there is still no report on the geochemical significance of the benzo[b]naphthothiophenes in oils up to now.

The ratio of benzo[a]carbazole/(benzo[a]carbazole + benzo[c] carbazole) (abbreviated as [a]/([a]+[c])) in oils has been successfully applied as an empirical measurement for determining the relative secondary migration distances of oils. The main mechanism is that more rod-shaped benzo[a]carbazole relative to the sub-spherical benzo[c]carbazole is preferentially removed from oils onto clay minerals and into solid organic matter in the carrier bed (Larter et al., 1996). As suggested by Larter et al. (1996), functionalized aromatic compounds with polarity/shape differences between isomers may be suitable molecular indicators for monitoring
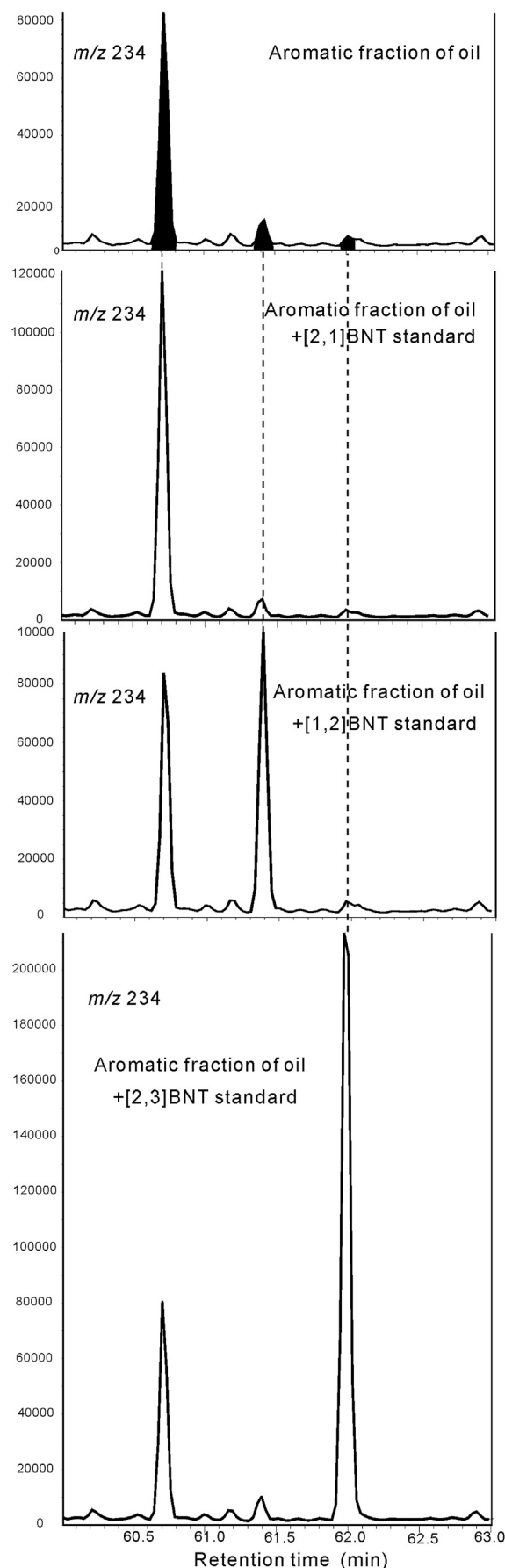
oil migration. Here benzo[b]naphtho[2,1-d] thiophene ([2,1]BNT) and benzo[b]naphtho[1,2-d] thiophene ([1,2]BNT) meet such requirements. Similar to dibenzothiophene, the sulfur atom on [2,1] BNT and [1,2]BNT can also form a hydrogen bond with the hydrogen atoms in the solid organic matter to produce dipole–dipole interaction with polar compounds in the carrier beds, and result in oil migration fractionation similar to that observed for dibenzothiophenes and benzocarbazoles.

4.2. Ratio of [2,1]BNT/([2,1]BNT+[1,2]BNT) variations during migration

Figure 6 shows the correlation of the ratio [a]/([a]+[c]) with the ratio [2,1]BNT/([2,1]BNT+[1,2]BNT) for data sets derived from oils in two different petroleum systems: one from the Tarim Basin, Northwest China; the other from the Fushan Depression, Beibuwan Basin, Southern China Sea. These two petroleum systems have been comprehensively studied with well-established secondary migration directions (Li et al., 2008a,b; Wang et al., 2008). The exact migration distances may not be known; however, the relative migration distance can be defined by referring to the nearest well as approximately 1 km. For example, the Ordovician oil reservoir in the Tahe oil field has been charged sourced by a source kitchen on the south side of this area, most probably at the Shuntuoguole Lower Uplift just between the Manjiaer and Awati Depressions (Wang et al., 2008). We define the distance for the well (Well Tp12CX) that is located nearest to the postulated source kitchen along the oil migration orientation as approximately 1 km (similar to that by Larter et al., 1996).

The ratio of [2,1]BNT/([2,1]BNT+[1,2]BNT) (BNT ratio) exhibits a generally positive linear correlation with benzo[a]carbazole/(benzo[a]carbazole + benzo[c] carbazole) (BCA ratio: [a]/([a]+[c])) with a correlation coefficient of 0.68 for data set 1 (Fig. 6a), which indicates that the relative concentration of the benzo[b]naphthothiophene (BNT) isomers may also be constrained by the same migration fractionation effects exerted on the benzocarbazole (BC) isomers. The variations may result from the differences of the nature and mineral compositions of the carrier beds and the intensity of the hydrogen bond between S—H … X and N—H … X (X is the oxygen atom in most cases). For example, increased abundance of clay minerals such as montmorillonite in the carrier bed and/or carboxyl group of organic matter can provide excess oxygen atoms to form hydrogen bonds with the pyrrolic nitrogen compounds. As mentioned above, the dipole moment of DBT is less than that of carbazole, which may result in a relatively lower S … H hydrogen bond energy and thus, likely weak adsorptive ability. Furthermore, apart from the effect of the chemical properties of dibenzothiophenes (DBTs) and benzo[b]naphthothiophenes (BNTs), the formation of S … H hydrogen bond primarily depends on the quantity and features of the H atoms, which is largely controlled by the type and abundance of organic matter in the carrier bed and/or other materials containing H— X bonds (X is an atom with high electronegativity). The overall positive linear relationship between the BCA ratio and the BNT ratio, however, suggests that the observed migration fractionation effect of the BNTs is similar to that of the BCAs. In contrast, the BNT ratios for oils from the Beibuwan Basin, South China Sea do not have as strong of a linear relationship with BCA ratios (Fig.6b). This may result from particularly low BNTs concentrations (Table 2).

Figure 4. Example mass chromatograms (*m/z* 234) of sample and standards for the identification of [2,1]BNT, [1,2]BNT and [2,3]BNT in oils. [2,1]BNT: Benzo[b]naphtho[2,1-d] thiophene; [1,2]BNT: Benzo[b]naphtho[1,2-d] thiophene, [2,3]BNT: Benzo[b]naphtho[2,3-d] thiophene.
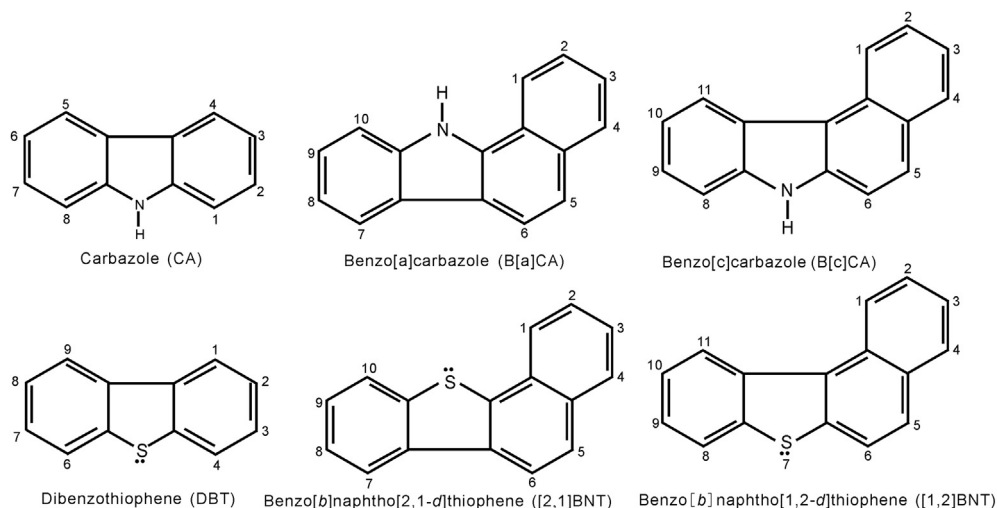
Figure 5. Structures of benzo[*b*]naphtho[2,1-*d*] thiophene ([2,1]BNT) and benzo[a] carbazole (B[a]CA), benzo[b]naphtho[1,2-*d*] thiophene ([1,2]BNT) and Benzo[*c*]carbazole (B[*c*] CA). Chemical structures and numbering system of [2,1]BNT, [1,2]BNT and [2,3]BNT are referenced from published literature (Karcher et al., 1985) .

The general trend for the BNT ratio obtained from the oils from typical carbonate source rocks in the Tarim Basin decreases with increasing migration distance (Fig. 7). It decreases from about 0.9 to 0.65 as the relative migration distance increases from 1 to 50 km (Table 3). The BNT ratio exhibits a strong linear relationship with relative migration distance in this petroleum system. The BNT ratios for the light oils and condensates from the Beibuwan Basin, South China Sea are generally higher than those of the oils from the Tarim Basin, indicating relatively shorter migration distances (less than 15 km). Compared to the Tarim Basin oils, the BNT ratios for the Beibuwan Basin oils exhibit a weaker linear relationship with the BCA ratio (Fig. 7). This may result from the inaccurate estimations of relative migration distances from this kind of oil reservoirs that migrated from adjacent source kitchens with short migration distances.

4.3. Concentrations of DBTs and BNTs variations during migration

The concentrations of [2,1]BNT, [1,2]BNT plus [2,3]BNT range from 14 to 89 μg/g oil with an average of 32 μg/g oil in oils (Table 3) from the carbonate source rocks in the Tarim Basin, which is about

one order of magnitude higher than that of the total concentrations of benzo[*a*]carbazole plus benzo[*c*]carbazole (ranging from 0.83 to 6.08 μg/g oil with an average of 3.35 μg/g oil). The concentrations of total dibenzothiophene, methyl-, dimethyl-, and trimethyl-thiophenes, benzo[b]naphtho[2,1-*d*]thiophene, and benzo[b] naphtha[1,2-*d*]thiophene in the oils analyzed range from 214 to 2116 μg/g oil, with an average of 973 μg/g oil. This is ten times higher than the concentrations of the total pyrrolic nitrogen compounds (total CAs and BCAs) in oils originated from carbonate source rocks in the Tarim Basin. The concentrations of the total DBTs and BNTs in oils from the lacustrine siliciclastic source rocks range from 23 to 476 μg/g oil with an average of 204 μg/g oil in the Fushan Depression, Beibuwan basin, South China Sea (Table 2). This value is about one-fifth the concentration of these compounds in the oils from the carbonate source rocks in the Tarim Basin, but is still higher than the pyrrolic nitrogen compounds (with an average value of 61 μg/g oil) (Table 2).

The concentrations of total DBTs plus BNTs for oils from the Tarim Basin tend to be positively correlated with those of the carbazoles plus the benzocarbazoles (Fig. 8a). Therefore, it seems that the variations of absolute concentrations of dibenzothiophenes
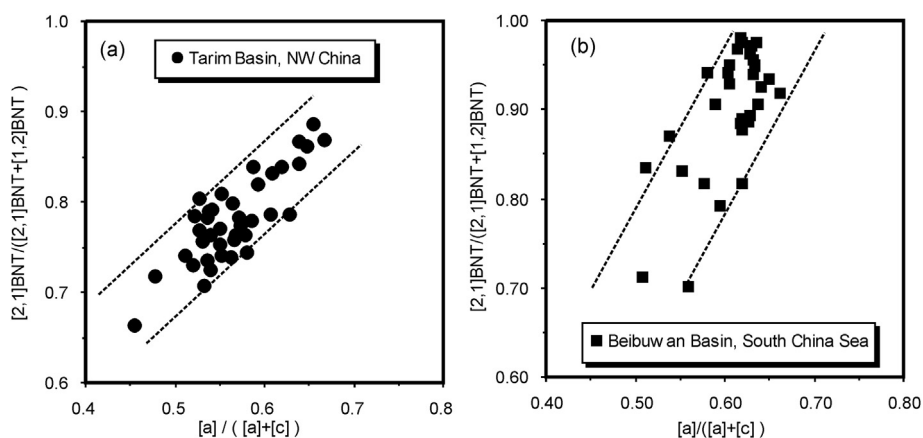

Figure 6. Plots of [2,1]BNT/([2,1]BNT+[1,2]BNT) (BNT ratio) and [a]/([a]+[c]) (BCA ratio) of oils from Tahe oil field, Tarim Basin (a), and oils and condensates from the Fushan Depression, Beibuwan Basin, Southern China Sea (b). The [2,1]BNT/([2,1]BNT+[1,2]BNT) is defined as the ratio of benzo[b]naphtha[2,1-*d*]thiophene/(benzo[b]naphtha[2,1-*d*] thiophene + benzo[b]naphtha[1,2-*d*]thiophene), whereas the [a]/([a]+[c]) is defined as the ratio of benzo[a]carbazole/(benzo[a]carbazole + benzo[c]carbazole). The Tahe oils show a linear relationship ($R^2 = 0.68$).
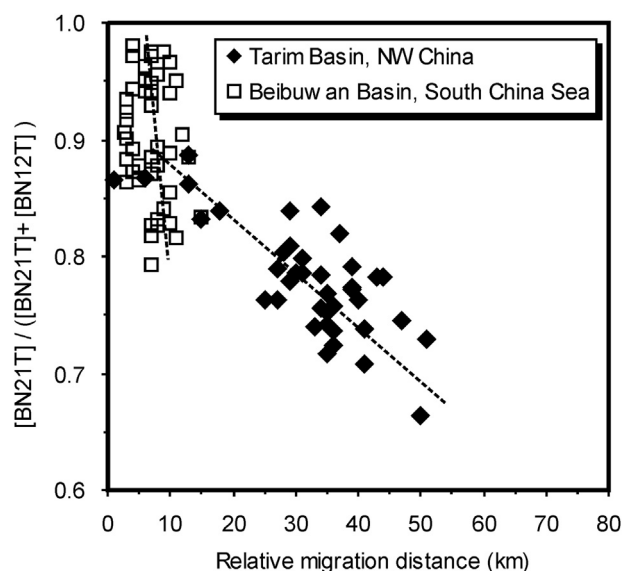
Figure 7. The BNT ratio for reservoired oils from the Tahe oil field, Tarim Basin and oils and condensates from the Fushan Depression, Beibuwan Basin plotted against the best estimates of secondary migration distance relative to a reference oil nearest to the source rock. The reference oil is given an arbitrary migration distance of 1 km.

(and benzo[b]naphthothiophenes) and carbazoles (and benzocarbazoles) in these oils are constrained by common factors. However, the concentrations of DBTs plus BNTs for oils from the Beibuwan Basin do not show an apparent positive correlation with those of CAs and BCAs. Some oil samples such as wells Hd1-1, H7, H5 and H3-2 etc. deflect away from the positive tendency (Fig. 8b). In comparison with the samples with similar total contents of DBTs, these samples have relatively lower total carbazoles contents, which may be caused by the low content of non-hydrocarbons in these light oils and condensates (Li et al., 2008a). Large errors can be easily caused during the process of separation of pyrrolic nitrogen compounds from other compound classes in oils, resulting in inaccurate total carbazole and benzocarbazole concentrations.

In order to facilitate comparisons, the concentrations of DBTs plus BNTs in individual oil samples have been normalized to the highest concentration of DBTs plus BNTs that is observed for each respective data set. Figure 9 shows the variations in the normalized concentration of the total DBTs plus BNTs as a function of relative migration distance for oils from the Tarim and the Beibuwan Basins. It shows that the concentrations of the DBTs plus BNTs decrease with increasing secondary migration distance with a general linear trend (correlation coefficient R^2 of 0.71) for the oils from the Tarim Basin (Fig. 9a). The concentrations of DBTs plus BNTs for light oils and condensates from the Beibuwan Basin show no significant correlation with relative migration distances (Fig. 9b). As previously discussed, this may result from the inaccurate estimation of relative migration distance. For oil accumulations in this lacustrine rift basin, the migration distances are relatively short. Oil reservoirs mainly occur around individual hydrocarbon generation centers. Thus, the relative migration distance that is determined by reference to a specific well can be inaccurate.

Unlike [2,1]BNT/([2,1]BNT+ [1,2]BNT), both the concentrations of BNTs and BCAs are less well-correlated with migration distance than the results described by Larter et al. (1996). This may be the result of the small numbers of data points in the two data sets examined in this study. The cases presented here are from typical Paleozoic cratonic basins and faulted Cenozoic rift basins, where the maximum migration distance is generally less than 100 km

(Wang et al., 2008). In foreland basins, the maximum migration distance can reach several hundreds of kilometers (Larter et al., 1996), and the benzo[a]carbazole plus benzo[c]carbazole concentrations can vary over two orders of magnitude (from 0.02 to over 4 μg/g oil) (Larter et al., 1996). This indicates that longer migration distances can result in stronger fractionation effects on the benzocarbazoles. The concentrations of the DBTs plus BNTs for the Tarim and Beibuwan Basin data sets, however, vary only up to four and twenty fold, respectively. The diminished molecular fractionation effect may be the result of the relatively short secondary migration distances. Furthermore, the trace quantity of the BNTs and the BCAs in the oils may result in greater analytical errors. In contrast the ratios of [[2,1]BNT]/([[2,1]BNT]+[[1,2]BNT]) or [a]/([a]+[c]) are more accurate with less experimental errors.

4.4. Effects of source rock maturity

An ideal migration-distance indicator should be solely influenced by migration processes and not by the thermal maturity, depositional environment, or source input of organic matter. As mentioned above, maturity can have marked effects on the distribution of molecular isomers of alkylated dibenzothiophenes. For example, according to the values of the enthalpy of the formation of DMDBTs, the stability of the 1,4-DMDBT is similar to that of the 2,4-DMDBT, which is much less than the 4,6-DMDB (Richard, 2001). With increasing maturity, the 4,6-DMDBT/1,4-DMDBT ratios should be elevated due to the increase in the amount of thermally stable isomers (Radke, 1988; Chakhmakhchev et al., 1997; Kruge, 2000).

The source of the DBTs in oils and sediments has been debated for several decades. The formation of the alkylated DBTs from sulfurized triterpenoid precursors, by the insertion of sulfur into polycyclic aromatic hydrocarbons such as alky biphenyls, was reported (Asif et al., 2009). Dibenzothiophenes are more stable than thiophenes and are the main polycyclic sulfur aromatics (Ho et al., 1974; Hughes, 1984; Santamaría-Orozco et al., 1998) within the main phase of the oil-generation window.

Santamaría-Orozco et al. (1998) found that the concentration of DBT exhibits a bimodal distribution, with the two maxima discernable around 0.71% and 0.91% R_o.

The basic geochemical features in samples from well SG1 in the Bohai Basin are listed in Table 4. They are lacustrine shales and dominated by Type II kerogen. The total organic carbon (TOC) content ranges from 1.37 wt.% to 3.27 wt.% with an average of 1.88 wt.%.

The 4-/1-MDBT (methyldibenzothiophene ratio: 4-methyldibenzothiophene/1-methyldibenzothiophene) increases with depth, which is similar to the trend of T_{max} (Table 4). The top of the oil-generation window for SG1 profile is about 2850 m (Fig. 10), corresponding to the T_{max} of 435 °C and C_{31} hopane 22S/(22S + 22R) of 0.54 (Table 4).

The total concentrations of DBTs (DBTs + BNTs) in source rock extracts are very low (about 20 μg/g C_{org} or less) at the burial depth shallower than 2850 m, and increase slowly to 40 μg/g C_{org} at a burial depth of 3100 m. The concentrations increase to about 118 μg/g C_{org} around 3300 m (Fig. 10a), which is roughly in agreement with the beginning of intensive oil generation. The entire trend of the total concentration of DBTs exhibits a bimodal distribution with two maxima around 3300 m and 3750 m. The concentrations of BNTs fit the same trend (Fig. 10a). Even though the bimodal distribution remains unproven because sampling densities are too low, it is clear that the total absolute concentrations of the DBT, MDBTs, DMDBTs plus TMDBTs or BNTs seem to exhibit no marked variations with maturity within the main oil-generation window (Santamaría-Orozco et al., 1998).

Table 3

Summary of carbazoles, C_1 to C_3 alkylcarbazoles, benzocarbazoles, dibenzothiophene, C_1 to C_3 alkyldibenzothiophenes and benzonaphthothiophenes of oils from the Tahe oil field, Tarim Basin.

Sample code	Concentration of CAs and BCAs (µg/g oil)						Concentration of DBTs and BNTs (µg/g oil)						[a]/([a]+[c])	[2,1]BNT/ ([2,1]BNT+[1,2]BNT)	Relative migration distance (km)
	CA	MCA	DMCA	TMCA	BCA	N	DBT	MDBT	DMDBT	TMDBT	BNT	S			
H1	4.15	24.74	63.72	30.62	0.82	124.07	52.89	114.41	114.79	50.50	7.33	339.92	0.63	0.95	6
H1-1	2.78	18.81	50.35	24.49	0.96	97.38	42.45	85.10	88.36	37.69	7.57	261.17	0.63	0.96	6
H2	1.66	9.26	25.24	12.48	0.34	48.99	16.78	39.47	42.18	16.78	2.30	117.50	0.58	0.94	6
H2-1	3.23	18.82	53.31	27.84	0.74	103.94	36.66	83.68	101.94	45.52	8.00	275.80	0.61	0.93	7
H2-2	4.01	21.69	56.27	28.25	1.55	111.77	34.84	67.38	77.24	34.33	5.99	219.78	0.62	0.97	7
H2-3	1.83	10.08	26.58	13.07	0.31	51.87	18.52	38.63	33.38	14.16	1.80	106.48	0.63	0.95	7
H3	1.73	15.62	50.46	27.30	1.15	96.26	37.01	78.28	82.78	36.05	6.57	240.70	0.63	0.96	8
H3-1	3.96	24.86	68.28	35.13	2.11	134.33	52.18	101.69	116.25	49.05	10.10	329.27	0.63	0.97	7
H3-2	3.87	26.56	75.02	37.76	2.24	145.45	32.17	66.49	71.22	32.89	5.21	207.98	0.63	0.98	9
H3-3	4.99	28.57	75.91	37.93	2.08	149.48	59.58	112.41	122.71	59.31	10.36	364.38	0.63	0.94	10
Hx4	1.62	12.99	43.22	25.18	1.28	84.30	35.60	66.93	69.40	30.31	6.77	209.00	0.61	0.97	10
Hx4	1.05	6.96	20.96	10.97	0.36	40.29	16.47	30.84	30.28	10.10	1.89	89.58	0.61	0.95	11
H5	0.17	2.15	14.02	12.58	0.47	29.39	33.93	74.45	75.00	30.91	4.02	218.32	0.60	0.94	7
H7	0.96	8.06	21.62	9.19	0.77	40.61	41.95	111.40	109.05	36.72	6.17	305.29	0.63	0.97	4
H7	0.60	4.10	8.98	2.95	0.33	16.96	36.59	108.09	115.72	41.35	7.47	309.22	0.62	0.98	4
Hd1	0.82	7.19	28.18	16.64	0.81	53.64	33.01	73.70	79.49	14.15	1.15	201.50	0.64	0.92	3
Hd1-1	0.69	5.52	23.16	14.62	0.95	44.95	38.89	88.23	87.58	172.62	5.32	392.63	0.65	0.93	3
H4-3	4.07	23.14	69.88	33.61	4.73	135.44	35.63	76.95	98.56	50.34	13.93	275.41	0.62	0.88	13
H8-1x	4.57	18.08	40.16	17.30	4.52	84.63	30.93	96.93	159.51	171.24	17.18	475.80	0.64	0.91	2.5
Hd1-4x	2.15	10.18	22.91	9.14	1.34	45.73	17.74	45.33	49.87	25.52	5.05	143.51	0.66	0.92	3
L1	4.42	15.05	36.40	11.70	2.35	71.35	12.08	25.19	40.45	23.53	5.27	106.51	0.54	0.87	7
L11	4.58	12.16	26.02	8.79	1.05	52.60	15.73	22.85	30.22	18.24	2.45	89.49	0.51	0.83	15
L1-2x	2.72	14.39	37.66	14.22	2.36	69.91	18.70	35.96	40.67	20.09	7.69	123.11	0.59	0.90	12
L4	2.11	8.98	20.41	6.64	1.15	39.30	6.06	12.48	13.58	6.55	2.68	41.34	0.62	0.89	10
L8x	7.06	34.82	95.89	41.29	9.94	189.00	15.24	44.72	80.09	57.53	14.00	211.58	0.58	0.82	11
L9x	1.18	5.80	18.66	10.03	1.35	37.02	9.96	38.07	68.74	48.99	8.56	174.31	0.55	0.83	8
H10	0.33	3.13	13.78	9.26	0.79	27.30	31.27	69.78	78.28	42.92	9.64	231.88	0.63	0.89	8
H2-13	0.28	2.09	8.12	6.24	0.73	17.46	16.01	32.80	46.19	24.97	7.05	127.02	0.59	0.79	7
H2-16	0.83	5.98	18.51	9.86	0.70	35.89	22.22	50.04	67.43	36.48	8.28	184.65	0.62	0.82	7
H2-17X	2.60	12.24	31.90	14.14	1.71	62.59	39.97	92.71	117.06	59.83	16.45	326.03	0.62	0.88	8
H2-18a	0.80	6.78	22.22	12.90	1.95	44.64	20.74	56.58	66.46	24.84	9.15	177.76	0.63	0.89	7
H2-5	0.23	1.17	2.95	1.29	0.12	5.76	2.71	7.20	8.56	3.87	0.68	23.03	0.61	0.83	7
H2-6	0.96	4.87	13.14	6.60	0.68	26.25	13.90	36.84	47.81	21.65	5.02	125.21	0.62	0.83	8
H3-12x	0.60	4.60	14.77	7.51	1.38	28.86	21.16	49.89	69.18	33.68	8.89	182.80	0.57	0.84	9
H3-5	0.22	1.50	6.11	5.27	0.41	13.50	14.43	31.86	41.04	20.42	4.45	112.20	0.65	0.85	10
H3-6	1.00	7.42	26.11	17.41	2.90	54.84	35.01	77.16	108.18	53.30	16.07	289.72	0.64	0.83	10
H8-1	4.57	18.08	40.16	17.30	4.52	84.62	22.99	72.72	107.02	57.09	12.47	272.30	0.64	0.88	3
Hd1-5	0.93	6.05	15.58	6.05	1.43	30.05	8.29	21.12	26.21	11.19	1.86	68.69	0.60	0.86	3
Hd1-6	0.04	0.30	1.20	0.71	0.21	2.46	12.32	39.05	45.58	18.29	3.55	118.79	0.60	0.89	4
Hd1-7	0.51	1.98	4.22	1.87	0.20	8.78	5.78	15.72	19.68	8.81	1.72	51.72	0.61	0.87	4
Hd4	2.08	7.23	12.00	3.34	1.21	25.86	17.96	81.79	118.87	49.18	17.76	285.56	0.64	0.94	4
Hd4-2	1.98	8.75	18.71	7.00	0.95	37.39	17.65	47.47	58.50	27.25	5.56	156.43	0.63	0.87	5
Hd4-3	2.71	11.28	22.59	8.69	1.89	47.15	29.34	83.95	119.89	63.01	11.28	307.48	0.61	0.88	5
Hd5	2.60	11.72	23.56	8.98	1.56	48.42	13.06	61.43	102.10	46.74	14.71	238.03	0.63	0.90	3

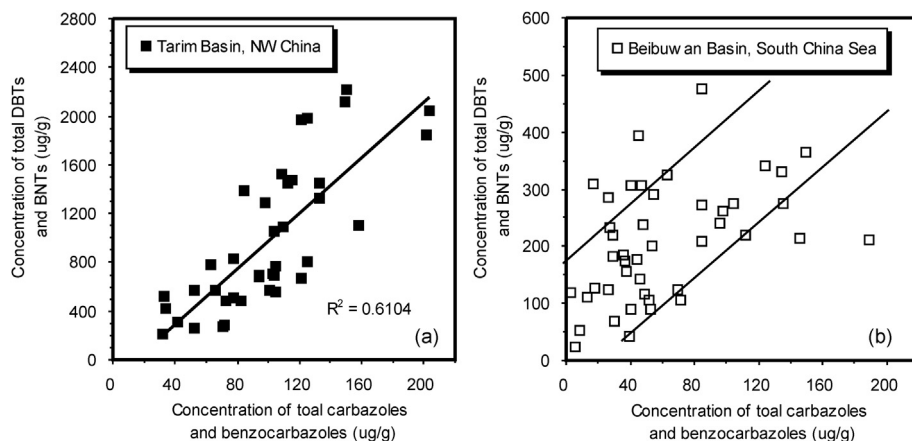Note: the definition of geochemical parameters same as Table 2.

Figure 8. Plots of the absolute concentration of total dibenzothiophene compounds (DBTs and BNTs) and carbazole compounds (carbazoles and benzocarbazoles) of oils from (a) Tahe oil field, Tarim Basin and (b) oils and condensates from the Fushan Depression, Beibuwan Basin, Southern China Sea.
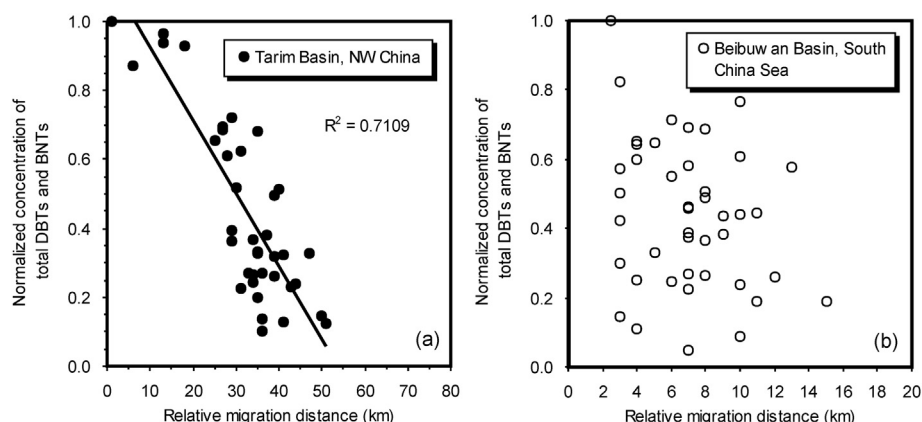
Figure 9. Normalized concentration of dibenzothiophene, alkyldibenzothiophenes, and benzonaphthothiophenes (DBTs + BNTs) as a function of relative migration distance for oils originated from (a) Tahe oil field in the Tarim Basin and (b) Beibuwan Basin, South China Sea. To facilitate comparisons, the concentrations have been normalized to that of the oil in each data set used with the highest concentration of (DBTs + BNTs). The Tahe oils show a linear relationship ($R^2 = 0.61$).

The [2,1]BNT/([2,1]BNT+[1,2]BNT) ratio of source rock extracts from Well SG1 shows no strong relationship with source maturity in the range of 430−440 °C (T_{max}) (equivalent to a burial depth of 3200 m−4000 m). The value for samples with a burial depth less than 3100 m, is about 0.70, which roughly corresponds to the beginning of the main oil-generation depth in this basin. It increases to 0.86 and then keeps constant with increasing maturity (Fig. 10b). This indicates that the BNT ratio may be constant within the main oil generation stage and that any variations in BNT ratio for mature oils related to the variations in source maturity are small compared to the variations caused by oil migration.

4.5. Effects of source input and depositional environment

Compositions of organic matter in source rocks or depositional environment are also important factors controlling the relative and absolute concentrations of most molecular markers. The relative concentration of dibenzothiophene to phenanthrene is closely related to depositional environment of organic matter

(Hughes et al., 1995). Oils or organic matter from marine carbonate, marl, or lacustrine sulfate-rich environments are typically enriched in dibenzothiophenes and their alkyl derivatives. In contrast, those oils or organic matter from low-sulfate marine or lacustrine shale, deltaic, or fluvial environments are characterized by lower concentrations of DBT and its alkyl DBTs (Hughes et al., 1995).

Huang and Pearson (1999) also observed that some DBT-based parameters are influenced by depositional environment. For example, high methyldibenzothiophene ratios (MDR) are associated with freshwater source deposition while low MDRs are found in oils of hypersaline source affinity (Huang and Pearson, 1999). The absolute concentrations of DBTs in oils derived from marine-carbonate source rocks in the Tarim Basin average 973 μg/g oil, which is five times higher than concentrations in the oils from the Beibuwan Basin, South China Sea, where the source rocks were deposited in a terrestrial input-dominated freshwater environment. Therefore, source rock depositional environments can exert a dominant influence when their range of variation is large.

Table 4
Selected geochemical parameters of Eocene source rocks from Well SG1, Western Depression, Bohai Bay Basin.

Sample No.	Depth (m)	TOC(%)	EOM mg/g C$_{org}$	T_{max} (°C)	HI mg/g C$_{org}$	OI mg/g C$_{org}$	Pr/Ph	C$_{31}$ Hopane$_e$ 22S/(22S + 22R)	MDR	DBT (μg/g C$_{org}$)	BNT (μg/g C$_{org}$)	[2,1]BNT/([2,1]BNT+[1,2]BNT)
SG04	2314.0	1.37	55.11	432	172	100	0.73	0.30	1.76	13.05	1.55	0.77
SG05	2352.0	1.44	40.80	435	164	93	0.71	0.28	1.68	6.37	0.99	0.76
SG06	2404.0	1.72	25.72	433	235	73	0.74	0.38	1.73	4.65	1.18	0.79
SG07	2459.0	1.93	59.38	431	329	52	0.53	0.49	1.24	5.62	1.67	0.65
SG08	2485.0	2.24	42.99	430	356	53	0.44	0.46	1.28	6.79	0.89	0.57
SG09	2518.0	2.11	45.97	430	409	61	0.43	0.47	1.59	5.76	0.64	0.56
SG11	2653.0	1.83	41.51	433	296	83	0.63	0.49	1.85	7.54	1.06	0.71
SG12	2672.0	1.92	61.70	434	391	75	0.56	0.44	1.99	15.30	1.44	0.67
SG13	2730.0	1.91	66.43	434	359	83	0.72	0.49	2.69	20.38	2.14	0.71
SG14	2783.0	1.86	60.89	435	354	120	0.75	0.51	2.14	21.64	1.92	0.65
SG15	2815.0	1.90	66.73	434	336	74	1.09	0.54	2.56	19.41	2.83	0.74
SG16	2888.0	1.76	74.46	435	354	78	1.02	0.54	2.61	25.32	2.06	0.68
SG17	2914.0	1.78	62.46	437	312	56	1.02	0.56	2.64	20.25	2.17	0.69
SG18	2956.0	1.77	67.38	437	298	99	0.99	0.56	2.26	19.87	2.05	0.65
SG19	3111.0	2.13	84.32	437	345	80	1.40	0.56	2.43	40.03	3.33	0.72
SG20	3239.0	1.99	138.26	437	319	91	1.18	0.56	2.88	78.90	103.10	0.85
SG21	3306.0	3.27	377.20	435	274	64	1.43	0.57	2.89	117.72	212.33	0.84
SG22	3372.0	1.87	170.68	439	294	86	1.11	0.55	2.99	110.10	90.63	0.86
SG25	3752.0	1.72	200.81	441	233	108	1.30	0.59	3.45	162.20	198.38	0.86
SG26	3819.0	1.64	151.90	439	213	122	1.23	0.58	3.74	98.97	197.00	0.86
SG27	4052.0	1.42	109.23	438	202	113	1.25	0.56	4.40	74.57	65.43	0.86

TOC: total organic carbon; EOM: extractable organic matter; T_{max}: temperature of maximum S$_2$ peak from Rock Eval pyrolysis; HI: hydrogen index (mg HC/g organic carbon); OI: oxygen index (mg HC/g organic carbon); 4-/1-MDBT: 4-methyldibenzothiophene/1-dibenzothiophene; DBT: concentration of total dibenzothiophene compounds; BNT: concentration of total benzo[b]naphthothiophenes. The definition of other parameters is referenced to Tables 1 and 3
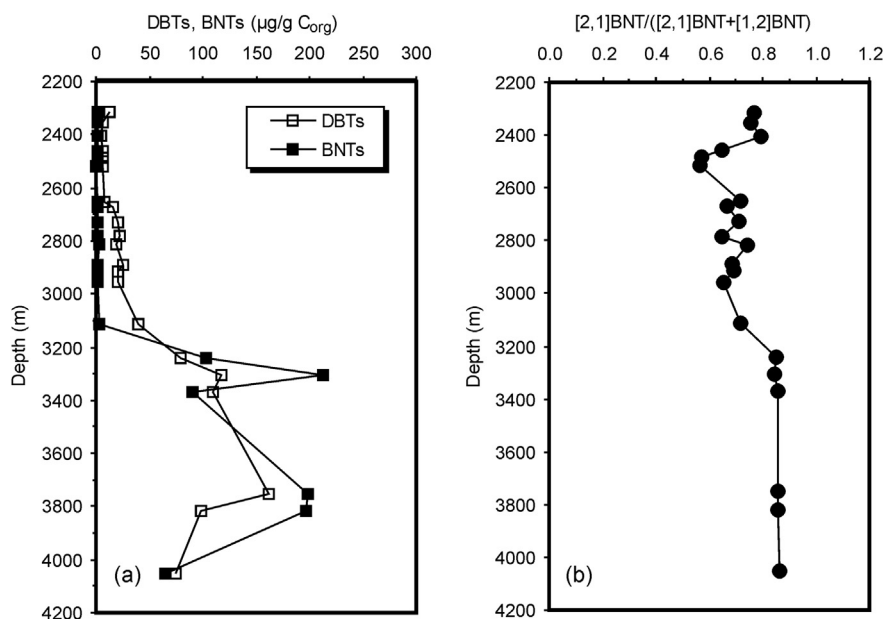
Figure 10. Depth-trend plot of (a) absolute concentrations of DBTs and BNTs, and (b) 2,1]BNT/([2,1]BNT+[1,2]BNT) (BNT ratio) in source rock extracts in well SG1 from the Western Depression, Bohai Bay Basin. Concentrations of BNT and DBT are quite low above the top of oil-generation window (about 2850 m), and increase abruptly at the beginning of the intensive hydrocarbon generation stage.

The prerequisite for tracing oil-migration distances by molecular markers is that all reservoired oils are derived from the same source bed/kitchen. Namely, all oils studied should belong to the same oil family. Therefore, the relative or absolute concentration of some compounds is mainly controlled by the oil-migration fractionation. Minor depositional environment variations may exist, but drastic changes can be excluded for oils generated within the main oil-generation stage. In addition, entrapped oils in reservoirs are a mixture of hydrocarbons generated by a range in organic matter composition in source rocks. The mixing process can reduce the minor variations of depositional environment. Thus, the factors of source input and depositional environment can be neglected for oils from the same oil family.

5. Conclusions

In this study, we have examined three isomers of benzo[b]naphthothiophenes to investigate the effects of petroleum migration fractionation on the geochemistry of sulfur heterocyclic aromatic compounds. Based on the results of this study, the following conclusions have been reached:

(1) Both the hydrogen bond and the dipole—dipole interaction mechanism theoretically explain the fractionation effect of dibenzothiophenes during the oil migration process. Although some differences exist, the fractionation effect is verified by analogy with carbazoles, which have a similar chemical structure and behavior during oil-migration processes. A novel polycyclic aromatic sulfur heterocyclic geochemical indicator — absolute concentrations of dibenzothiophenes (dibenzothiophene and its alkyl derivatives, isomers of benzo[b]naphthothiophene) — is suggested to trace oil-migration distances.

(2) Benzo[b]naphtha[2,1-d]thiophene and benzo[b]naphtha[1,2-d]thiophene have similar chemical structures to benzo[a]carbazole and benzo[c]carbazole respectively. These two isomers have different interaction with carrier bed media

and can cause migration fractionation during secondary oil migration. A novel molecular parameter, the BNT ratio (abbreviated as [2,1]BNT/([2,1]BNT+[1,2]BNT)), is proposed to estimate the relative oil-migration distances.

(3) Variations of thermal maturity may influence the relative concentrations of different isomers of dibenzothiophenes. However, the BNT ratio is constant within the main oil-generation stage, which suggests that any variations in BNT ratio for mature oils related to variations in source maturity are small compared to the variation caused by migration. The absolute concentration of DBTs plus BNTs is approximately constant for immature samples and dramatically increases to a maximum at a maturity corresponding to the onset of the main oil-generation window. Variations of maturity within the main oil-generation stage exert no marked influence on absolute concentrations of DBTs plus BNTs.

(4) The organic matter type and depositional environment of source rocks are main factors controlling the concentrations of DBTs and BNTs in corresponding oils. However, variations in the concentrations of DBTs and BNTs for oils from the same source rock/kitchen are minor. Thus the variations of DBTs and BNTs concentrations in oils are mainly controlled by migration fractionation.

(5) The advantages of DBTs and BNTs over carbazoles and benzocarbazoles in the study of oil migration are (1) they are usually more abundant than carbazoles and benzocarbazoles in oils, and especially light oils and condensates, and (2) they can be obtained by conventional GC—MS analysis of aromatic fractions.

Acknowledgments

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