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Distribution and geochemical significance of alkylbenzenes for crude oil with different depositional environments and thermal maturities

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A R T I C L E   I N F O

A B S T R A C T

A total of 45 alkylbenzenes were detected and identified in crude oils with different depositional environments and thermal maturities from the Tarim Basin, Beibuwan Basin, and Songliao Basin using comprehensive two-dimensional gas chromatography time-of-flight mass spectrometry (GC × GC-TOFMS). By analyzing the distribution characteristics of C_0–C_5 alkylbenzenes, it is found that the content of some alkylbenzenes varies greatly in crude oils. Based on the distribution characteristics of 1,2,4,5-tetramethylbenzene (TeMB) and 1,2,3,4-TeMB, the ratio of 1,2,4,5-TeMB to 1,2,3,4-TeMB is proposed to indicate the organic matter origin and depositional environment of ancient sediments. Oil samples originated mainly from lower hydrobiont, algae, bacteria and source rocks deposited under reducing/anoxic conditions have low 1,2,4,5-/1,2,3,4-TeMB values (less than 0.6), while oil samples originated mainly from terrestrial higher plants and source rocks deposited under oxic/sub-oxic conditions have higher 1,2,4,5-/1,2,3,4-TeMB values (greater than 1.0). The significant difference of 1,2,4,5-/1,2,3,4-TeMB values is controlled by 1,2,4,5-TeMB content. 1,2,4,5-TeMB content in oils derived from source rocks deposited in oxidized sedimentary environment (greater than 1.0 mg/g whole oil) is higher than that in oils from source rocks deposited in reduced sedimentary environment (less than 1.0 mg/g whole oil). 1,2,4,5-/1,2,3,4-TeMB ratio might not or slightly be affected by evaporative fractionation, biodegradation and thermal maturity. 1,2,4,5-/1,2,3,4-TeMB ratio and 1,2,4,5-TeMB content can be used as supplementary parameter for the identification of sedimentary environment and organic matter input. It should be noted that compared to the identification of organic matter sources, the 1,2,4,5-/1,2,3,4-TeMB parameter is more effective in identifying sedimentary environments.

1. Introduction

Monoaromatic hydrocarbons are known as alkylbenzene, which is an important component in crude oils (Zhang et al., 2014a; Cheng et al., 2015a), source rock extracts (Summons and Powell, 1987), and the pyrolysate of kerogen (Lis et al., 2008), coal (Gallegos, 1981) and asphaltene (Hartgers et al., 1994a; Jia et al., 2007; 2008), especially for light oils and condensates with extremely abundant alkylbenzene compounds (2–6 w.t.%) (Ostroukhov et al., 1983). Alkylbenzenes are mainly formed by carbon-carbon bond cleavage of aromatic moiety linked to macromolecular compounds (Hartgers et al., 1994a). Alkylbenzene parameters were used to distinguish organic matter source (Hartgers et al., 1994b, 1994c), depositional environment (Sinninghe Damsté et al., 1993), thermal evolution (Lis et al., 2008) and secondary alteration (Volkman et al., 1984; Connan, 1984; Thompson, 1987, 1988).

1,2,3-trimethylbenzene (TMB) and 1,3- + 1,4-dimethylbenzene (DMB) are formed by the aromatization of nonaromatic carotenoids during diagenesis stage (Hartgers et al., 1994a). 1,2,3,4-tetramethylbenzene (TeMB) can be derived from not only carotenoids (Requejo et al., 1992) but also algal lipids (Pedentchouk et al., 2004). 1,2,3,4-TeMB usually has a relatively negative $\delta^{13}C$ value (−23‰~−24‰), indicating a strongly reduced water environment with a relatively high concentration of H_2S (Jia et al., 2007, 2008). The ratio of 1,2,3,5-TeMB to 1,2,3,4-TeMB and the concentration of 1,2,3,5-TeMB were considered to be indicative of depositional environment of ancient sediments (Cheng et al., 2015a). A

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series of evaluation parameters for the maturity of C_4-alkylbenzenes have been proposed by Hill et al. (2004). There is a good positive correlation between some alkylbenzenes parameters, which might be related to the maturity of crude oils (Zhang et al., 2014a; Cheng et al., 2015a). Toluene/n-heptane (Tol/nC_7) is usually used to indicate whether oils is affected by evaporative fractionation (Thompson, 1987; 1988).

Although the origin, distribution and application of alkylbenzens have been reported in previous literatures, as there are many types of alkylbenzene compounds, they still contain a lot of geochemical information to discriminate the source of organic matter and sedimentary environment of light oils and condensates to be excavated. In addition, previous studies usually used gas chromatography-mass spectrometry (GC-MS) with poor separation effect to separate alkylbenzene in crude oils, while comprehensive two-dimensional gas chromatography time-of-flight mass spectrometry (GC × GC-TOFMS) with good separation effect paid less attention to the separation of alkylbenzene in crude oils (Cheng et al., 2015a, 2015b). With the help of Nist 11.0 and published literatures (Cheng et al., 2015a), a total of 45 alkylbenzenes were identified by GC × GC-TOFMS in crude oils with different depositional environment and thermal maturities. The main reasons for the significant differences in the C_0–C_5 alkylbenzenes distribution of different sedimentary basins are analyzed, and the potential indicators of sedimentary environment, organic matter source, and thermal maturity in crude oils will be discussed.

2. Samples and methods

2.1. Samples

Crude oil samples, with different depositional environments and thermal maturities, were collected from three sedimentary basins (Tarim Basin, Beibuwan Basin and Songliao Basin) in China (Fig. 1a). The types of crude oil samples, the age of the reservoir, the age of the source rock and the depositional environment of the source rock has been shown in Table 1 in detail.

2.1.1. Tarim Basin oils

The Tabei Uplift is one of the structural units that enrich oil and gas in the Tarim Basin (Fig. 1b) (Song et al., 2015). In this study, 15 crude oils were taken from Ordovician reservoirs in the Halahatang depression and marginal areas. The data of molecular markers indicate that crude oils come from the Cambrian-Ordovician source rocks (Wang et al., 2008). The geochemical indicators of maturity indicate that the source rocks are in a mature stage (Chang et al., 2013). Although the origin of all studied oils from the Tarim Basin remain controversial, these oils are derived from marine source rocks with a reduced sedimentary environment (Chang et al., 2013).

2.1.2. Beibuwan Basin oils

Located in the north of Hainan Island, the Fushan Depression is a Cenozoic depression of the Beibuwan Basin, with an area of 2920 km^2 (Fig. 1c) (Li et al., 2007). In this study, nine oil samples were derived from the Fushan Depression of the Beibuwan Basin, including seven oil samples from the Huachang Oilfield, one oil sample from the Huadong Oilfield and one oil sample from the Chaoyang Oilfield, respectively. All the studied samples from Beibuwan Basin are originated from the mudstone of the Liushagang Formation (E_2l) with high organic matter abundance, which were deposited in a strongly oxidized sedimentary environments (Li et al., 2008, 2009). The CPI (Carbon preference index), C_{29}-sterane 20S/(20S + 20R) and C_{31}-hopane 22S/(22S + 22R) values show that all these oils are generated from mature organic matter (Li et al., 2007).

2.1.3. Songliao Basin oils

In Fig. 1d, the Shuangcheng-Taipingchuang is situated in the northeast of the Songliao Basin, consisted of the Sanzhao Depression, Chaoyanggou Terrace, Changchunling Anticlinal Zone, and Bingxian-Wangfu Depression (Wang et al., 2009a). In this study, 16 oil samples, with intermediate density, high viscosity, high wax contents, low sulfur contents, and high freezing point, were sampled from the Shuangcheng-Taipingchuan area. Crude oils from the Shuangcheng-Taipingchuan area are derived from the Cretaceous lacustrine facies mudstone deposited under reducing/anoxic conditions (Wang et al., 2009b). The maturity parameters of sterane and hopane indicate that the crude oils is in a low to medium mature stage (Wang et al., 2009a).

2.2. Methods

2.2.1. Gas chromatography-mass spectrometry (GC-MS)

All crude oils were separated into saturated hydrocarbons, aromatic hydrocarbons, NSO hydrocarbons and asphaltenes by column chromatography. When the saturated and aromatic hydrocarbons were analyzed by Agilent 6890 GC linked with Agilent 5979i MS, the GC equipped with HP-5MS (60 m × 0.25 μm × 0.25 μm). The programmed temperature settings for GC-MS analysis of saturated hydrocarbons were as follows: initially, the GC oven temperature was 50 °C, maintained for 1 min, and then heated to 100 °C at 20 °C/min, and then to 310 °C at 3 °C/min, and retained for 10 min. The programmed temperature settings for GC-MS analysis of aromatic hydrocarbons were as follows: the GC oven originally temperature was set at 80 °C and held for 1 min, and programmed at 3 °C/min to 310 °C, and finally held for 20 min. Helium was used as a carrier gas and the voltage of the ion source was set as 70 eV.

2.2.2. Comprehensive two-dimensional gas chromatography time-of-flight mass spectrometry (GC × GC-TOFMS)

The GC × GC-TOFMS consisted of Agilent 7890 GC linked with Pegasus 4D TOFMS. The chromatographic column is composed of two chromatographic columns with opposite phases, which are a non-polar capillary column HP-PONA (50 m × 0.20 mm × 0.50 μm) in the first dimension and the polar capillary column Rxi-17 (1.7 m × 0.1 mm × 0.1 μm) in the second dimensions. The temperature setting of the first dimensional chromatography column was set as follows: the initial oven temperature was set to 35 °C, and held for 5 min, and then to 295 °C at 2 °C/min and held for 30 min. The temperature setting of the second dimensional chromatography column was set as follows: the initial oven temperature was set to 40 °C, and held for 5 min, and then to 280 °C at 2 °C/min and held for 30 min. The modulation period was 6 s with 1.2 s hot pulse time. The detector and ion source ionization voltages were 1350 V and 70 eV, respectively. The temperature of the transmission line and the ion source were set to 280 °C and 250 °C, respectively. Helium was used as carrier gas. Chroma TOF software version 4.71 was used for data acquisition and processing.

3. Results and discussion

3.1. Identification of C_0–C_5 alkylbenzenes in crude oil

As shown in Fig. 2, the distribution of C_0–C_5 alkylbenzenes were demonstrated on the total ion chromatogram and sum ion chromatogram of RP14-5X oil from the Tarim Basin. The aromatic hydrocarbons appear above n-alkanes, branched alkanes and cycloalkanes, because compound separation is based on compound boiling point and polarity in the first and second dimension, respectively. Besides, the compounds are dominated by n-alkanes,
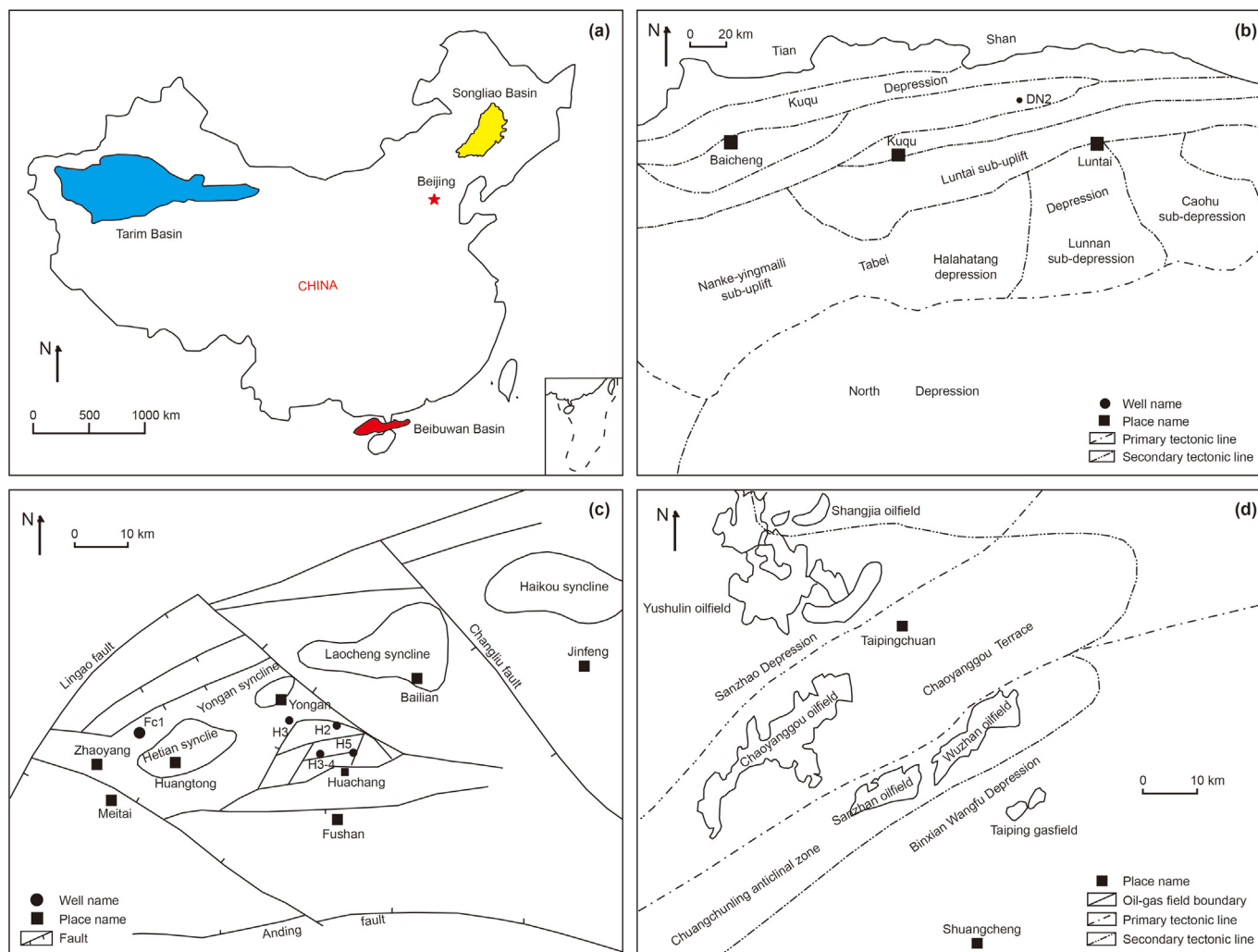
Fig. 1. (a) The distribution of the studied basin in China; (b—d) showing the basic geological structure of the northern Tarim Basin, the Fushan Depression in the Beibuwan Basin and the Shuangcheng-Taipingchuan area in the Songliao Basin, respectively.

cycloalkanes, branched alkanes and alkylbenzenes (Fig. 2a). With the help of Nist 11.0 and published literatures (Cheng et al., 2015a), a total of 45 alkylbenzenes were identified in crude oils, including benzene, toluene, three C_2 alkylbenzene isomers, eight C_3 alkylbenzene isomers, twenty-two C_4 alkylbenzene isomers, and ten C_5 alkylbenzene isomers, respectively (Fig. 2b, Table 2).

In this study, the mass chromatogram of m/z 78, 92, 106, 120, 134, 148 show benzene, toluene, C_2 alkylbenzene isomers, C_3 alkylbenzene isomers, C_4 alkylbenzene isomers, and C_5 alkylbenzene isomers, respectively. With alkylbenzene carbon number increasing, the C_0—C_5 alkylbenzenes exhibit en echelon distribution based on the boiling point and polarity of the compound (Fig. 2b). The 1,3- + 1,4-DMB present co-elution in crude oils by GC × GC-TOFMS analysis, which is consistent with previous studies (Hartgers et al., 1992). The total peak area of co-eluted compound is used to indicate their combined contents. The *tert*-butylbenzene, with very low contents in the Beibuwan Basin oils and Songliao Basin oils, was below the detection limit in the Tarim Basin oils.

3.2. Distribution of C_6—C_{13} hydrocarbon compounds and C_0—C_5 alkylbenzenes in crude oils

In this study, the C_6—C_{13} hydrocarbon compounds and C_0—C_5 alkylbenzenes were quantified by the known amounts of internal standard (1-hexene) in crude oils. The concentrations of C_6—C_{13} hydrocarbon compounds are 631.5 mg/g whole oil, 603.6 mg/g whole oil and 179.6 mg/g whole oil in the Tarim Basin oils, Beibuwan Basin oils and Songliao Basin oils, respectively (Fig. 3a). It is consistent with the former research results that the light hydrocarbon compounds make up about 30% in crude oils from the Songliao Basin, up to 90% in light oils and condensates from the Tarim Basin and Beibuwan Basin (Hunt et al., 1980). The concentrations of total C_0—C_5 alkylbenzene compounds are 56.1 mg/g whole oil, 108.1 mg/g whole oil and 7.6 mg/g whole oil in the Tarim Basin oils, Beibuwan Basin oils and Songliao Basin oils, respectively (Fig. 3a). It proves the previous results that the monocyclic aromatic hydrocarbons in crude oils can account for 2—6 w.t.% (Ostroukhov et al., 1983). Because of the Tarim Basin oils and Beibuwan Basin oils with similar thermal evolution, the difference in C_6—C_{13} hydrocarbon compounds concentrations of the Tarim Basin oils and Beibuwan Basin oils were mainly controlled by sedimentary environment and the origin of organic matter. However, compared with the Tarim Basin oils and Beibuwan Basin oils, the relatively low concentrations of C_6—C_{13} hydrocarbon compounds and total C_0—C_5 alkylbenzenes from the Songliao Basin oils are mainly controlled by thermal maturity. The difference in total C_0—C_5 alkylbenzenes

Table 1
Basic geological and geochemical information for all studied oils.

No.	Name	Location	Type of oil	Reservoir age	Source age	Depositional environment of source rock	References
1	RP14-5X	Tarim	Light oil	O	O−Є	Marine	Zhang and Huang (2005)
2	RP8-1	Tarim	Light oil	O	O−Є	Marine	As above
3	RP8001	Tarim	Light oil	O	O−Є	Marine	As above
4	XK501C	Tarim	Light oil	O	O−Є	Marine	As above
5	XK8-1	Tarim	Light oil	O	O−Є	Marine	As above
6	JY103C	Tarim	Light oil	O	O−Є	Marine	As above
7	JY5H	Tarim	Light oil	O	O−Є	Marine	As above
8	YM1	Tarim	Light oil	O	O−Є	Marine	As above
9	YM2	Tarim	Light oil	O	O−Є	Marine	As above
10	YM3	Tarim	Light oil	O	O−Є	Marine	As above
11	YM4	Tarim	Light oil	O	O−Є	Marine	As above
12	YM5	Tarim	Light oil	O	O−Є	Marine	As above
13	YM102	Tarim	Light oil	O	O−Є	Marine	As above
14	YJ1X	Tarim	Light oil	O	O−Є	Marine	As above
15	YJ2X	Tarim	Light oil	O	O−Є	Marine	As above
16	H1-01	Beibuwan	Light oil	E	E	Lacustrine	Li et al. (2008, 2009)
17	H1-02	Beibuwan	Light oil	E	E	Lacustrine	As above
18	H2	Beibuwan	Light oil	E	E	Lacustrine	As above
19	H2-3	Beibuwan	Light oil	E	E	Lacustrine	As above
20	H3	Beibuwan	Light oil	E	E	Lacustrine	As above
21	H5-01	Beibuwan	Light oil	E	E	Lacustrine	As above
22	HX4-01	Beibuwan	Light oil	E	E	Lacustrine	As above
23	FCl-02	Beibuwan	Light oil	E	E	Lacustrine	As above
24	HD-1-1	Beibuwan	Light oil	E	E	Lacustrine	As above
25	Chang64	Songliao	Heavy oil	K	K	Lacustrine	Wang et al. (2009b)
26	Chang11-1	Songliao	Heavy oil	K	K	Lacustrine	As above
27	San501-1	Songliao	Heavy oil	K	K	Lacustrine	As above
28	Wu501-1	Songliao	Heavy oil	K	K	Lacustrine	As above
29	Wu105	Songliao	Heavy oil	K	K	Lacustrine	As above
30	Zhao940	Songliao	Heavy oil	K	K	Lacustrine	As above
31	Zhao631	Songliao	Heavy oil	K	K	Lacustrine	As above
32	Chuan10	Songliao	Heavy oil	K	K	Lacustrine	As above
33	Chuan8	Songliao	Heavy oil	K	K	Lacustrine	As above
34	Shu42	Songliao	Heavy oil	K	K	Lacustrine	As above
35	Shuang301	Songliao	Heavy oil	K	K	Lacustrine	As above
36	Shuang231	Songliao	Heavy oil	K	K	Lacustrine	As above
37	Shuang15	Songliao	Heavy oil	K	K	Lacustrine	As above
38	Shuang34	Songliao	Heavy oil	K	K	Lacustrine	As above
39	Shuang32	Songliao	Heavy oil	K	K	Lacustrine	As above
40	Shang2	Songliao	Heavy oil	K	K	Lacustrine	As above

Note: Є: Cambrian; O: Ordovician; E: Eocene; K: Cretaceous.

concentrations may be controlled by organic matter source and depositional environment in the Tarim Basin oils and Beibuwan Basin oils. Moreover, the striking difference in the concentrations of total C_0−C_5 alkylbenzenes in all studied oils are mainly related to C_2−C_4 alkylbenzenes contents (Fig. 3b).

In Fig. 4, the distribution of C_2 alkylbenzene isomers present in all studied oils is dominated by 1,3- + 1,4-DMB. The distribution of C_3 alkylbenzene isomers present in all studied oils is dominated by 1,2,4-TMB. The distribution of C_4 alkylbenzene isomers in the Beibuwan Basin oils are dominated by 1-M-3-PB and 1,2,3,5-TeMB, while the distribution of C_4 alkylbenzenes in the Tarim Basin oils and Songliao Basin oils are dominated by 1-M-3-PB and 1,2,3,4-TeMB. The 1,2,4,5-TeMB contents in the Tarim Basin oils and Songliao Basin oils from the source rocks with a reduced sedimentary environment (less than 1.0 mg/g whole oil) is lower than the Beibuwan Basin oils from the source rocks with a strongly oxidized sedimentary environments (greater than 1.0 mg/g whole oil) (Fig. 5a, Table 3). The 1,2,3,4-TeMB contents in the Tarim Basin oils and Beibuwan Basin oils is higher than the Songliao Basin oils (Fig. 5b, Table 3). The distribution of C_5 alkylbenzene in crude oils from the above three basins varies greatly. The content of C_5 alkylbenzene in the Tarim Basin oils is not significantly different, and the content of 1-E−3,4,5-TMB is the highest. The Beibuwan Basin oils have the highest content of 1-E−2,4,5-TMB, followed by 1,2,3,4,5-PMB. The content of C_5 alkylbenzene in crude oils from the

Songliao Basin is generally low, and the content of the PB is the highest.

Although the Tarim Basin oils, Beibuwan Basin oils and Songliao Basin oils have different sedimentary environments and thermal evolution, 45 alkylbenzenes display a similar distribution pattern, especially for some specific alkylbenzene isomers (Fig. 4). For example, 1-M-3-EB is higher abundance than both 1-M-4-EB and 1-M-2-EB in all studied oils. In addition, 1,2,4-TMB is higher abundance than both 1,3,5-TMB and 1,2,3-TMB in all studied oils. Moreover, 1-M-3-iPB and 1-M-4-iPB are much more abundant than 1-M-2-iPB in all studied oils. The formation of the above mentioned specific alkylbenzene may be mainly related to the way of breaking the carbon-carbon bond, but not related to the deposition environment and organic matter source of source rocks.

3.3. 1,2,4,5-/1,2,3,4-TeMB ratio as an indicator of sedimentary environment

Based on the significant differences of 1,2,4,5-TeMB and 1,2,3,4-TeMB concentrations (Fig. 5), 1,2,4,5-/1,2,3,4-TeMB ratio is proposed to indicate the sedimentary environments of ancient sediments. The two monoterpenes ratios (MT1 and MT2) were proposed to recognize the redox conditions of source rocks (Wang et al., 2014). The 2,6-dimethyloctane/2-methyl-3-ethylheptane (MTR) and 1,2,3,5-/1,2,3,4-TeMB (TeMBr) ratios were also proposed to
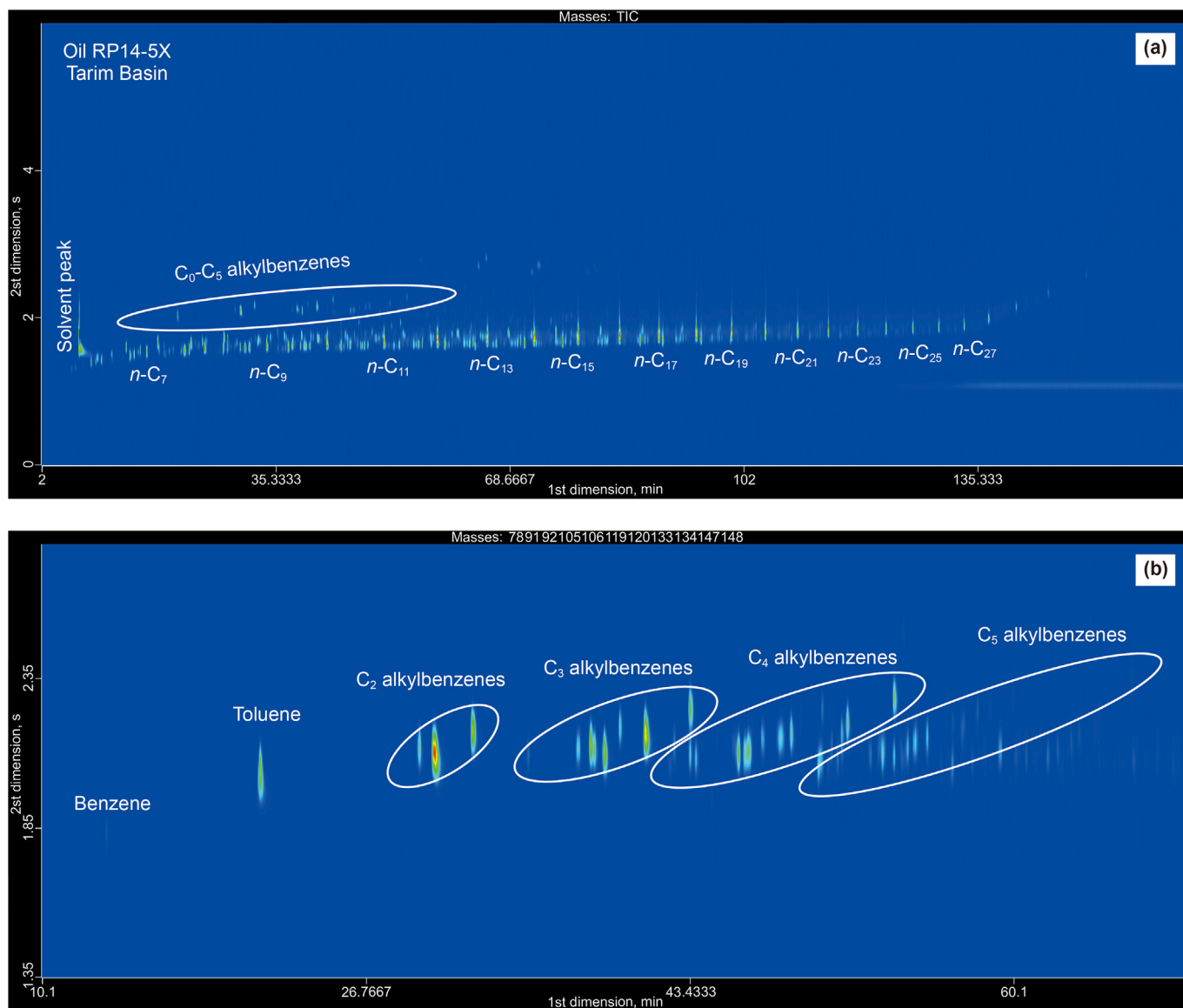
Fig. 2. The distributions of C_0−C_5 alkylbenzenes on (a) the total ion chromatogram and (b) summed mass chromatogram of oil RP14-5X from the Tarim Basin.

distinguish depositional environments of crude oils (Cheng et al., 2015a, 2015b). As shown in Fig. 6, based on MTR, MT1, MT2, TeMBr and 1,2,4,5-/1,2,3,4-TeMB values, all crude oil samples are divided into two groups. Oils derived from the Tarim Basin and Songliao Basin have relatively lower TeMBr values, higher MTR, MT1 and MT2 values corresponding to lower 1,2,4,5-/1,2,3,4-TeMB values (less than 0.6), which indicate crude oils from source rocks deposited in reduced sedimentary environment. In contrast, oils from the Beibuwan Basin have higher TeMBr values, lower MTR, MT1, and MT2 values as well as higher 1,2,4,5-/1,2,3,4-TeMB values (greater than 1.0), which imply crude oils from source rocks deposited in an oxidized deposition environment.

Pristine/Phytane (Pr/Ph) ratio was used to assess the redox sedimentary environments of ancient sediments (Peters et al., 2005). Generally, a higher Pr/Ph values indicates an oxidized deposition environment, while a lower Pr/Ph values indicates a reduced deposition environment (Peters et al., 2005). In Fig. 7, all studied oils and condensates can be divided into two groups based on Pr/Ph values and 1,2,4,5-/1,2,3,4-TeMB values. Oils derived from the Tarim Basin and Songliao Basin have relatively lower Pr/Ph

values (0.82−1.22) and 1,2,4,5-/1,2,3,4-TeMB values (0.10−0.58) (Table 3), which indicate their source rocks formed in reduced sedimentary environment. However, oils derived from the Beibuwan Basin have higher Pr/Ph values (2.93−4.46) and 1,2,4,5-/1,2,3,4-TeMB values (1.12−2.45) (Table 3), which imply their source rocks formed in an oxidized deposition environment. In general, oils with low 1,2,4,5-/1,2,3,4-TeMB values (less than 0.6) suggest source rock deposited under anoxic/reducing sedimentary conditions, whereas oils with higher 1,2,4,5-/1,2,3,4-TeMB values (greater than 1.0) indicate source rock deposited under oxic/sub-oxic sedimentary conditions.

3.4. 1,2,4,5-/1,2,3,4-TeMB ratio as an indicator of organic matter origin

The above difference can also be observed in the compositions of C_7 hydrocarbon fraction. The predominance of n-heptane (nC_7) usually indicate the input of marine organic matter, whereas the high proportion of methylcyclohexane ($MCyC_6$) is commonly related to terrigenous organic matter input (Ten Haven, 1996;

Table 2
A total of 45 alkylbenzenes were identified in crude oils by Nist 11.0 and Cheng et al. (2015b).

No	Compounds	BP[a]	1D[b]	1D RI[c]	2D[d]	Abbreviation
1	Benzene	78	14.1	646.2	1.87	Bz
2	Toluene	91	22.0	752.4	2.09	Tol
3	Ethylene	91	30.2	848.3	2.17	EB
4	1,3- + 1,4-Dimethylbenzene	91	30.9	856.3	2.15	1,3- + 1,4-DMB
5	1,2-Dimethylbenzene	91	31.0	857.5	2.16	1,2-DMB
6	Isopropylbenzene	105	35.8	912.8	2.15	iPB
7	n-propylbenzene	91	38.3	941.9	2.17	PB
8	1-methyl-3-ethylbenzene	105	39.0	950.0	2.19	1-M-3-EB
9	1-methyl-4-ethylbenzene	105	39.2	952.3	2.16	1-M-4-EB
10	1,3,5-Trimethylbenzene	105	39.7	958.1	2.16	1,3,5-TMB
11	1-methyl-2-ethylbenzene	105	40.5	967.4	2.26	1-M-2-EB
12	1,2,4-Trimethylbenzene	105	41.8	982.6	2.23	1,2,4-TMB
13	1,2,3-Trimethylbenzene	105	44.1	1010.0	2.33	1,2,3-TMB
14	tert-Butylbenzene	119	41.7	980.0	2.19	t-BB
15	2-Methylpropylbenzene	91	43.1	997.5	2.11	2-MPB
16	1-Methylpropylbenzene	105	43.2	998.8	2.17	1-MPB
17	1-Methyl-3-isopropylbenzene	119	44.1	1010.0	2.16	1-M-3-iPB
18	1-Methyl-4-isopropylbenzene	119	44.4	1013.8	2.14	1-M-4-iPB
19	1-Methyl-2-isopropylbenzene	119	45.5	1027.5	2.21	1-M-2-iPB
20	1,3-Diethylbenzene	119	46.3	1037.5	2.19	1,3-DEB
21	1-Methyl-3-propylbenzene	105	46.5	1040.0	2.16	1-M-3PB
22	1,4-Diethylbenzene	119	46.8	1043.8	2.19	1,4-DEB
23	1-Methyl-4-propylbenzene	105	46.9	1045.0	2.16	1-M-4-PB
24	n-Butylbenzene	91	46.9	1045.0	2.17	BB
25	1,3-Dimethyl-5-ethylbenzene	119	47.1	1047.5	2.17	1,3-DM-5-EB
26	1,2-Diethylbenzene	105	47.3	1050.0	2.25	1,2-DEB
27	1-Methyl-2-propylbenzene	105	47.8	1056.3	2.22	1-M-2-PB
28	1,4-Dimethyl-2-ethylbenzene	119	48.6	1066.3	2.23	1,4-DM-2-EB
29	1,3-Dimethyl-4-ethylbenzene	119	48.7	1067.5	2.23	1,3-DM-4-EB
30	1,2-Dimethyl-4-ethylbenzene	119	49.2	1073.8	2.24	1,2-DM-4-EB
31	1,3-Dimethyl-2-ethylbenzene	119	49.7	1080.0	2.30	1,3-DM-2-EB
32	1,2-Dimethyl-3-ethylbenzene	119	50.8	1093.8	2.31	1,2-DM-3-EB
33	1,2,4,5-Tetramethylbenzene	119	51.8	1106.6	2.24	1,2,4,5-TeMB
34	1,2,3,5-Tetramethylbenzene	119	52.1	1110.5	2.27	1,2,3,5-TeMB
35	1,2,3,4-Tetramethylbenzene	119	54.5	1142.1	2.37	1,2,3,4-TeMB
36	2-tert-Butylbenzene	92	52.0	1109.2	2.13	2-t-BB
37	4-tert-Butylbenzene	92	52.3	1113.2	2.12	4-t-BB
38	n-Pentylbenzene	91	54.9	1147.4	2.15	PB
39	1-Ethyl-2,4,6-trimethylbenzene	133	57.1	1176.3	2.27	1-E–2,4,6-TMB
40	1-Ethyl-2,4,5-trimethylbenzene	133	57.9	1186.8	2.26	1-E–2,4,5-TMB
41	1-Ethyl-2,3,5-trimethylbenzene	133	58.0	1188.2	2.28	1-E–2,3,5-TMB
42	1-Ethyl-3,4,5-trimethylbenzene	133	58.7	1197.4	2.30	1-E–3,4,5-TMB
43	1-Ethyl-2,3,6-trimethylbenzene	133	59.4	1207.0	2.34	1-E–2,3,6-TMB
44	1-Ethyl-2,3,4-trimethylbenzene	133	60.6	1223.9	2.38	1-E–2,3,4-TMB
45	1,2,3,4,5-Pentamethylbenzene	133	64.0	1271.8	2.40	1,2,3,4,5-PMB

Note: [a] Base peak. [b] The first dimensional retention time (min). [c] Retention index. [d] The second dimensional retention time, s.
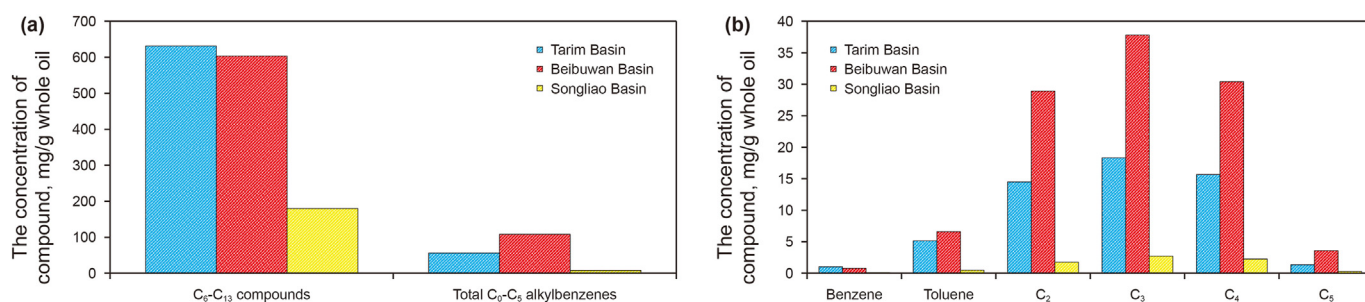

Fig. 3. (a) The $C_6–C_{13}$ light hydrocarbon compounds and total $C_0–C_5$ alkylbenzenes concentrations and (b) the $C_0–C_5$ alkylbenzenes contents in all studied oils from the different sedimentary basin.

Odden et al., 1998). Oils from carbonate sources have been found to contain the lowest amounts of the cycloalkanes (CyC_{5-7}) and the highest number of the n-alkanes (nC_{5-7}), whereas those bearing terrestrial organic matter contain the highest amounts of cyclo-alkanes and the lowest amounts of n-alkanes (Song et al., 2019). In Fig. 8, oils derived from the Beibuwan Basin have high CyC_{5-7}/nC_{5-7} values (1.95–6.87), low $nC_7/MCyC_6$ values (0.18–0.53), and high 1,2,4,5-/1,2,3,4-TeMB values (greater than 1.0), whereas oils derived from the Tarim Basin and Songliao Basin have lower CyC_{5-7}/nC_{5-7} values (0.50–0.73 and 0.69–2.14, respectively), higher $nC_7/MCyC_6$ values (1.64–2.04 and 0.72–1.59, respectively), and lower 1,2,4,5-/1,2,3,4-TeMB values (less than 0.6) (Table 3).
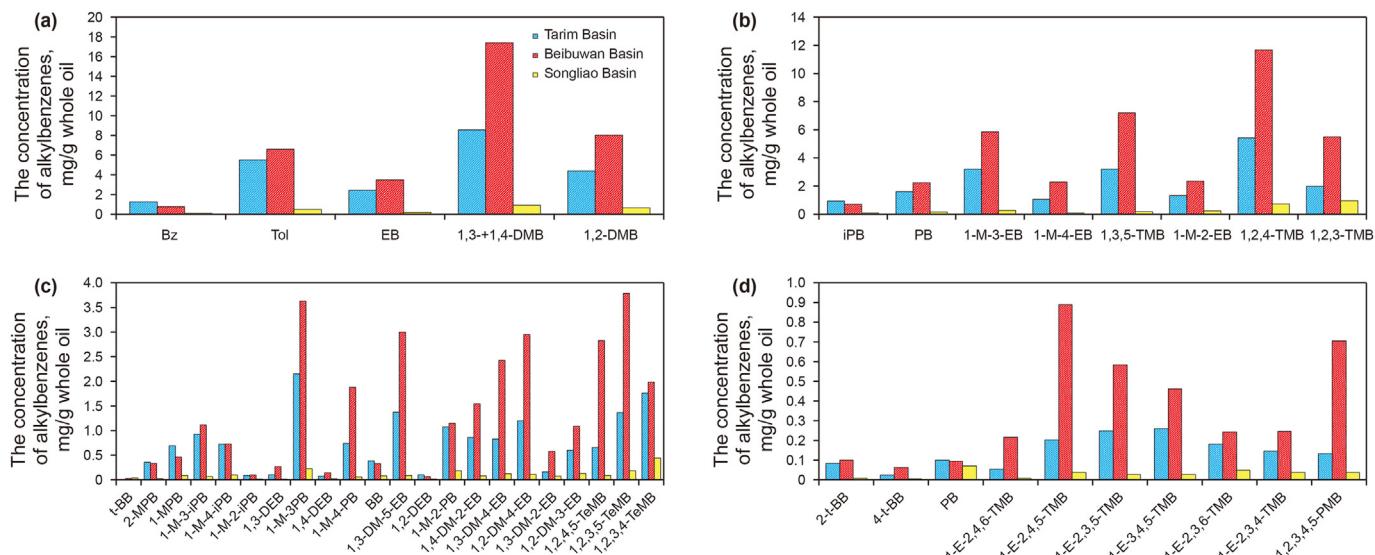
Fig. 4. The histogram of the concentrations of 45 alkylbenzene compounds for all studied oils. (a) representing Benzene, Toluene and three C₂ alkylbenzene isomers; (b−d) showing the eight C₃ alkylbenzene isomers, twenty-two C₄ alkylbenzene isomers, and ten C₅ alkylbenzene isomers, respectively. The abbreviation of the compound corresponds to the name of the compound in Table 2.
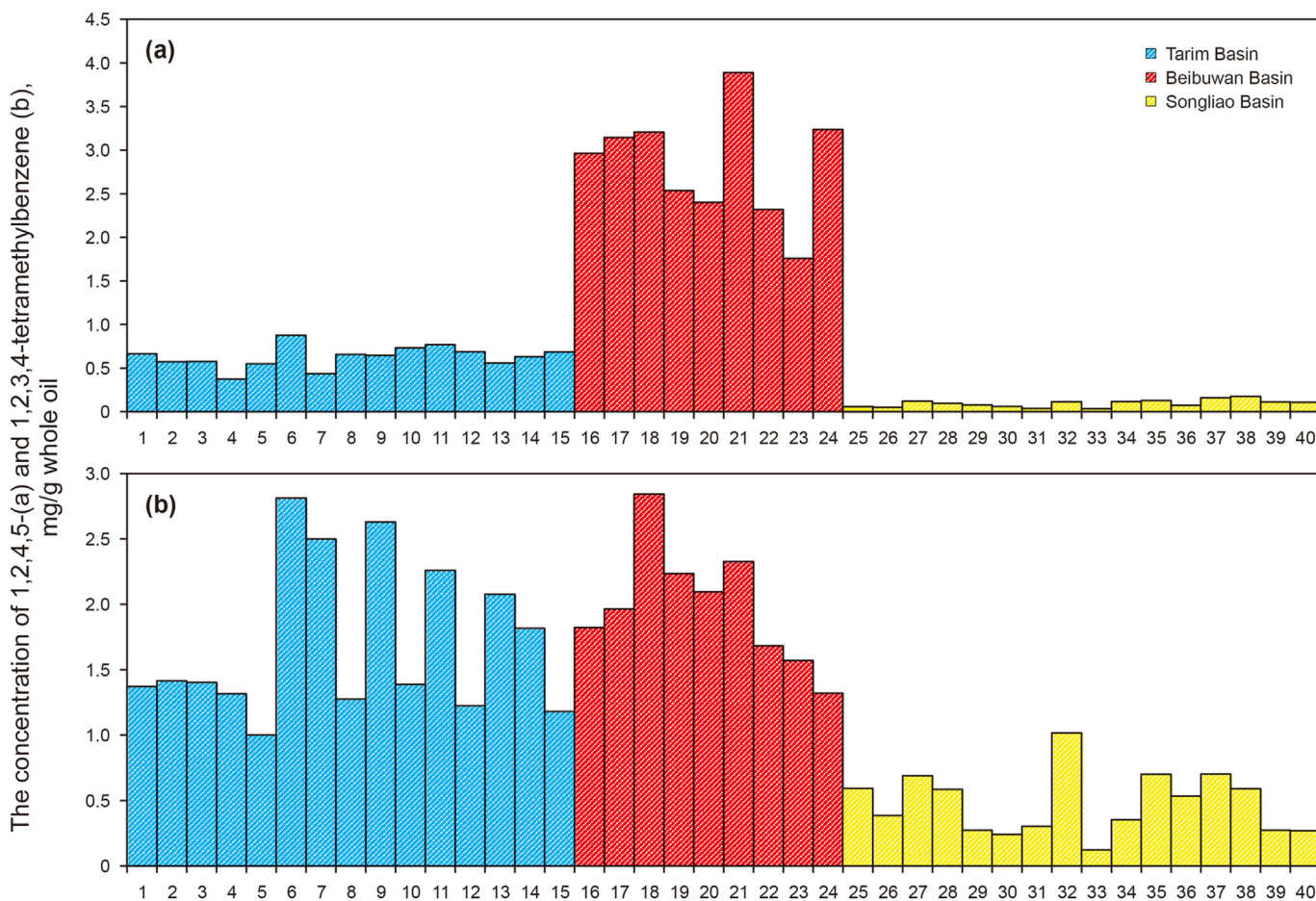

Fig. 5. The histogram of 1,2,4,5-tetramethylbenzene and 1,2,3,4-tetramethylbenzene concentrations for all studied oils.

The relative higher abundance bicyclic sesquiterpenes, including cadinane, 2,2,4a,7,8-pentamethyl-decalin, 1,2,2,5,5-pentamethyl-*trans*-decalin and 1,1,2,5,5-pentamethyl-*trans*- decalin, were usually used to indicate lacustrine organic matter origin (van Aarssen et al., 1992; Nytoft et al., 2009). In Fig. 9, oils derived from the Beibuwan Basin have high cadinane/

Table 3
Molecular marker parameters for all studied oils.

No.	Well	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
1	RP14-5X	0.48	0.66	1.37	0.98	0.90	1.44	1.24	0.86	1.71	0.64	0.17	0.09	0.03	0.45	0.35	0.09	0.90	37.62	2.29	9.72	0.91	9.78	0.91	0.47	0.27
2	RP8-1	0.41	0.57	1.42	0.88	0.66	1.20	0.88	0.78	1.75	0.58	0.20	0.11	0.07	0.57	0.40	0.07	0.81	37.33	2.48	7.44	0.88	9.12	0.90	0.46	0.26
3	RP8001	0.41	0.58	1.40	1.05	0.79	1.38	2.53	0.78	1.72	0.73	0.21	0.14	0.06	0.54	0.40	0.13	0.90	38.13	2.42	7.90	0.89	9.21	0.90	0.46	0.26
4	XK501C	0.29	0.38	1.32	0.85	1.07	1.90	0.81	0.63	1.64	0.58	0.19	0.08	0.01	0.30	0.27	0.07	0.62	34.90	2.20	6.13	0.86	6.44	0.87	0.47	0.27
5	XK8-1	0.55	0.55	1.00	0.94	0.96	1.65	1.02	1.05	1.73	0.56	0.22	0.09	0.05	0.54	0.40	0.12	0.52	37.24	2.30	13.98	0.93	12.11	0.92	0.49	0.28
6	JY103C	0.31	0.88	2.81	0.89	0.90	1.81	0.90	0.70	1.75	0.59	0.14	0.09	0.03	0.33	0.30	0.15	0.69	36.93	2.05	6.43	0.87	7.20	0.88	0.43	0.25
7	JY5H	0.17	0.43	2.50	0.82	0.90	1.86	1.24	0.50	1.79	0.59	0.14	0.09	0.03	0.38	0.31	0.11	0.69	38.19	1.93	5.28	0.84	7.15	0.88	0.41	0.24
8	YM1	0.51	0.66	1.28	0.98	0.67	1.30	1.07	1.02	1.72	0.55	0.23	0.17	0.06	0.71	0.47	0.06	1.59	36.69	2.23	15.57	0.94	12.56	0.93	0.51	0.30
9	YM2	0.25	0.65	2.63	0.91	0.90	1.63	1.13	0.58	2.04	0.52	0.08	0.07	0.01	0.30	0.26	0.16	0.72	39.97	2.00	5.99	0.86	7.14	0.88	0.42	0.25
10	YM3	0.53	0.73	1.39	0.93	0.77	1.39	0.87	1.03	1.74	0.60	0.26	0.14	0.07	0.65	0.47	0.15	1.36	38.14	2.28	15.28	0.94	12.65	0.93	0.50	0.30
11	YM4	0.34	0.77	2.26	0.97	0.70	1.27	3.29	0.70	1.98	0.50	0.17	0.09	0.05	0.40	0.31	0.22	0.77	39.26	2.15	8.72	0.90	8.52	0.89	0.48	0.28
12	YM5	0.56	0.69	1.22	0.87	0.61	1.05	1.02	1.03	1.75	0.52	0.25	0.13	0.06	0.75	0.50	0.18	0.81	37.07	2.26	16.46	0.94	13.19	0.93	0.51	0.30
13	YM102	0.27	0.56	2.08	0.92	0.75	1.46	1.46	0.69	1.98	0.53	0.11	0.08	0.02	0.28	0.25	0.22	0.71	38.94	1.92	8.02	0.89	7.92	0.89	0.46	0.27
14	YJ1X	0.35	0.63	1.82	0.90	0.76	1.30	0.97	0.71	1.86	0.54	0.26	0.10	0.09	0.36	0.27	0.18	0.77	38.00	2.20	7.85	0.89	8.78	0.90	0.45	0.26
15	YJ2X	0.58	0.68	1.18	0.95	0.93	1.68	0.73	1.08	1.77	0.51	0.31	0.13	0.08	0.61	0.44	0.21	1.24	37.51	2.39	13.82	0.93	12.47	0.93	0.50	0.29
16	H1-01	1.63	2.96	1.82	3.81	0.27	0.29	0.28	1.71	0.22	5.42	1.38	0.42	0.41	3.66	1.53	0.45	3.76	13.49	1.28	6.98	0.87	6.12	0.86	0.54	0.29
17	H1-02	1.60	3.15	1.96	3.73	0.35	0.31	0.25	1.71	0.40	2.25	0.80	0.16	0.33	1.71	1.18	0.38	3.19	18.37	1.27	6.26	0.86	5.50	0.85	0.52	0.28
18	H2	1.13	3.21	2.84	4.30	0.42	0.33	0.55	1.66	0.44	2.28	0.89	0.34	0.40	3.11	1.46	0.32	3.48	30.52	nd	5.65	0.85	6.00	0.86	0.51	0.28
19	H2-3	1.13	2.54	2.24	4.26	0.43	0.66	0.67	1.64	0.53	2.29	0.94	0.41	0.43	3.85	1.55	0.34	4.20	26.72	nd	6.54	0.87	5.75	0.85	0.53	0.28
20	H3	1.15	2.40	2.10	3.89	0.41	0.41	0.25	1.69	0.18	6.87	0.86	0.42	0.45	3.58	1.55	0.33	3.41	10.10	1.17	5.38	0.84	5.20	0.84	0.50	0.27
21	H5-01	1.67	3.89	2.33	4.46	0.23	0.21	0.05	2.40	0.41	2.83	0.77	0.55	0.62	4.06	1.28	0.60	3.15	21.41	1.06	5.30	0.84	5.97	0.86	0.47	0.24
22	HX4-01	1.38	2.32	1.68	4.46	0.18	0.18	0.22	2.04	0.48	1.91	0.61	0.40	0.38	2.99	1.34	0.50	3.77	21.07	1.32	5.71	0.85	6.17	0.86	0.45	0.24
23	FCl-02	1.12	1.76	1.57	2.93	0.39	0.48	0.22	1.84	0.26	4.72	0.61	0.23	0.35	2.63	1.31	0.29	2.17	14.25	0.95	3.73	0.79	4.84	0.83	0.44	0.23
24	HD-1-1	2.45	3.24	1.32	3.65	0.39	0.28	0.16	2.80	0.35	3.13	2.66	0.40	0.41	4.19	1.72	0.61	5.69	21.86	1.70	11.44	0.92	7.42	0.88	0.61	0.32
25	Chang64	0.10	0.06	0.59	1.20	1.89	2.81	1.19	0.30	0.74	1.89	0.05	0.12	0.08	0.58	0.77	0.01	0.60	26.11	0.65	3.07	0.75	3.21	0.76	0.36	0.18
26	Chang11-1	0.12	0.05	0.39	1.19	1.39	6.36	1.24	0.25	0.72	2.14	0.05	0.09	0.06	0.44	0.63	0.03	0.55	26.79	0.61	1.68	0.63	2.96	0.75	0.35	0.17
27	San501-1	0.18	0.12	0.69	1.12	1.27	2.34	1.04	0.36	0.74	1.75	0.07	0.05	0.00	0.32	0.67	0.01	0.57	28.00	0.69	2.59	0.72	3.28	0.77	0.34	0.18
28	Wu501-1	0.17	0.10	0.59	1.17	1.75	30.91	1.01	0.38	0.79	1.77	0.09	0.08	0.09	0.54	0.79	0.01	0.58	28.66	0.69	3.07	0.75	3.48	0.78	0.36	0.18
29	Wu105	0.29	0.08	0.27	1.17	1.45	2.73	1.19	0.52	0.87	1.46	0.09	0.08	0.05	0.52	0.74	0.06	0.55	32.51	1.13	3.05	0.75	4.38	0.81	0.32	0.17
30	Zhao940	0.25	0.06	0.24	1.20	1.30	2.40	0.83	0.47	1.15	1.13	0.08	0.06	0.01	0.39	0.58	0.00	0.68	40.59	1.57	3.46	0.78	5.64	0.85	0.25	0.13
31	Zhao631	0.13	0.04	0.30	1.10	1.92	27.47	1.00	0.32	0.85	1.56	0.08	0.04	0.01	0.32	0.55	0.01	0.61	32.82	1.04	2.41	0.71	3.77	0.79	0.31	0.16
32	Chuan10	0.11	0.11	1.02	1.18	1.60	3.15	0.98	0.31	0.85	1.60	0.09	0.05	0.00	0.25	0.54	0.01	0.58	29.49	0.91	1.71	0.63	2.97	0.75	0.33	0.16
33	Chuan8	0.29	0.04	0.12	1.12	1.54	2.29	0.91	0.76	1.35	0.92	0.06	0.08	0.02	0.45	0.68	0.01	0.59	42.68	1.64	6.25	0.86	5.73	0.85	0.33	0.18
34	Shu42	0.33	0.11	0.35	1.22	1.12	1.91	0.83	0.63	1.59	0.69	0.03	0.09	0.09	0.58	0.66	0.01	0.98	42.64	2.41	5.00	0.83	6.10	0.86	0.29	0.16
35	Shuang301	0.18	0.13	0.70	1.19	1.26	2.39	0.98	0.39	0.80	1.56	0.09	0.11	0.09	0.64	0.77	0.01	0.58	29.32	0.71	3.17	0.76	3.56	0.78	0.36	0.18
36	Shuang231	0.14	0.07	0.53	1.21	1.50	10.41	0.98	0.28	0.78	1.64	0.07	0.12	0.10	0.63	0.80	0.02	0.64	25.57	0.69	2.60	0.72	3.09	0.76	0.38	0.18
37	Shuang15	0.23	0.16	0.70	1.07	1.64	2.37	1.00	0.42	1.05	1.35	0.05	0.06	0.01	0.36	0.67	0.02	0.52	31.48	1.51	3.54	0.78	5.88	0.85	0.33	0.17
38	Shuang34	0.30	0.17	0.59	1.18	1.37	2.14	1.00	0.50	1.04	1.13	0.08	0.10	0.07	0.57	0.74	0.02	0.54	33.42	1.34	3.69	0.79	9.59	0.91	0.30	0.16
39	Shuang32	0.41	0.11	0.27	1.22	1.52	2.14	0.87	0.76	1.13	1.06	0.10	0.08	0.06	0.58	0.77	0.12	0.85	36.75	1.20	6.76	0.87	8.41	0.89	0.30	0.16
40	Shang2	0.40	0.11	0.27	1.22	1.67	2.60	0.85	0.69	1.49	1.00	0.01	0.06	0.06	0.37	0.56	0.07	0.77	41.22	1.66	6.26	0.86	4.65	0.82	0.42	0.17

Note: 1. 1,2,4,5-/1,2,3,4- Tetramethylbenzene; 2. 1,2,4,5-Tetramethylbenzene (mg/g whole oil); 3. 1,2,3,4-Tetramethylbenzene (mg/g whole oil); 4. Pristane/Phytane (Pr/Ph); 5. 2,6-Dimethyloctane/2-Methyl-3-ethylheptane (MTR); 6. 2-Methyl-3-ethylheptane/3-methylnonane (MT1); 7. 1,1,2,3-Tetramethylcyclohexane/Propylcyclohexane (MT2); 8. 1,2,3,5/1,2,3,4- Tetramethylbenzene (TeMBr); 9. nC_7/MCyC$_6$; 10. CyC$_{5-7}$/nC_{5-7}; 11.Tol/nC_7; 12. 2,2,4a,7,8-Pentamethyl-decalin/(2,2,4a,7,8-pentamethyl-decalin + 8β(H)-drimane); 13. Cadinane/(cadinane + 8β(H)-drimane); 14. 1,1,2,5,5-pentamethyl-trans-decalin/(1,1,2,5,5-pentamethyl-trans-decalin + 8β(H)-drimane); 15. 1,2,2,5,5-Pentamethyl-trans-decalin/(1,2,2,5,5-pentamethyl-trans-decalin + 8β(H)-drimane); 16. Oleanane/(Oleanane + C$_{30}$ Hopane); 17. (C$_{19}$TT + C$_{20}$TT)/C$_{23}$TT; 18. Heptane value; 19. Isoheptane value; 20. MDR: 4-/1-MDBT; 21. MDR': 4-/(4- + 1-MDBT); 22. EDR: 4,6-DMDBT/4-EDBT; 23. EDR': 4,6-DMDBT/(4,6-DMDBT + 4-EDBT); 24. F$_1$: (2-MP + 3-MP)/(2-MP + 3-MP + 1-MP + 9-MP); 25. F$_2$: 2-MP/(2-MP + 3-MP + 1-MP + 9-MP); TT: Tricyclic terpanes; CyC: Cycloalkanes; nC_7: n-heptane; MCyC$_6$: methylcyclohexane; Tol: Toluene. MP: Methyl Phenanthrene; MDBT: Methyldibenzothiophene; DMDBT: Dimethyldibenzothiophene; EDBT: Ethyl-dibenzothiophene; nd: no data; Items 1−3, 5−8 were obtained by GC × GC-TOFMS analysis, and other data were obtained by GC-MS analysis.
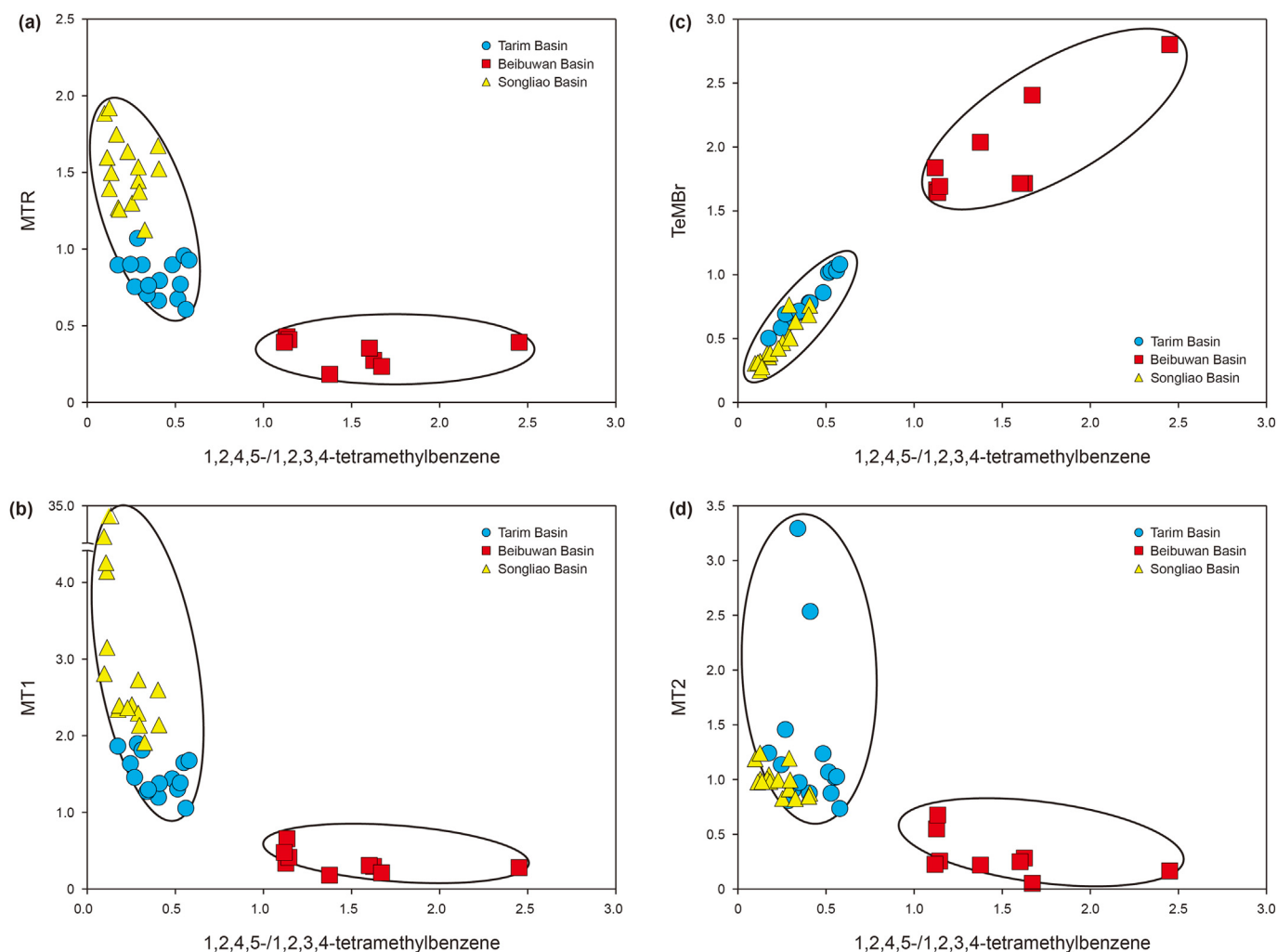
Fig. 6. The cross-plot of 1,2,4,5-/1,2,3,4-tetramethylbenzene vs. (a) 2,6-dimethyloctane/2-methyl-3-ethylheptane (MTR), (b) 2-methyl-3-ethylheptane/3-methylnonane (MT1), (c) 1,2,3,5/1,2,3,4- tetramethylbenzene (TeMBr), and (d) 1,1,2,3-tetramethylcyclohexane/propylcyclohexane (MT2) for all studied oils.
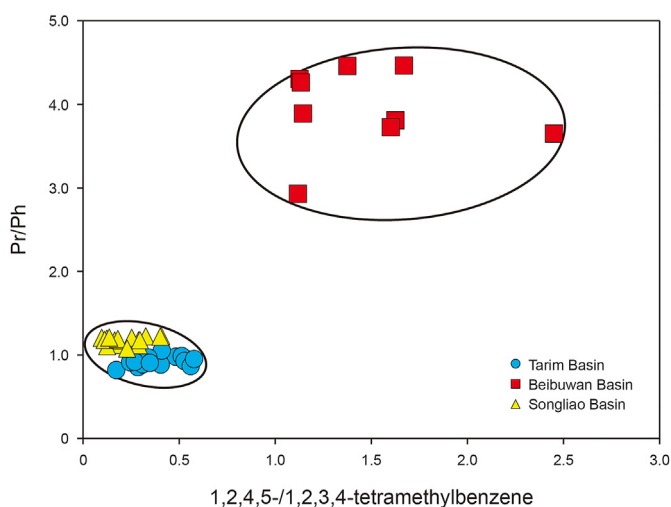

Fig. 7. The cross-plot of 1,2,4,5-/1,2,3,4-tetramethylbenzene vs. Pristane/Phytane (Pr/Ph) for all studied oils.

(cadinane + 8β(H)-drimane) values (0.33−0.62), 2,2,4a,7,8-pentamethyl-decalin/(2,2,4a,7,8-pentamethyl-decalin + 8β(H)-drimane) values (0.16−0.55), 1,2,2,5,5-pentamethyl-*trans*-decalin/8β(H)-drimane values (1.71−4.19), 1,1,2,5,5-pentamethyl-*trans*-decalin/8β(H)-drimane values (1.18−1.72) and 1,2,4,5-/1,2,3,4-TeMB values (greater than 1.0), whereas oils derived from the Tarim Basin and Songliao Basin have lower cadinane/(cadinane + 8β(H)-drimane) values (0.01−0.09 and 0−0.10, respectively), 2,2,4a,7,8-pentamethyl-decalin/(2,2,4a,7,8-pentamethyl-decalin + 8β(H)-drimane) values (0.07−0.17 and 0.04−0.12, respectively), 1,2,2,5,5-pentamethyl-*trans*-decalin/8β(H)-drimane values (0.25−0.50 and 0.54−0.80, respectively), 1,1,2,5,5-pentamethyl-*trans*-decalin/8β(H)-drimane values (0.28−0.75 and 0.25−0.64, respectively), and 1,2,4,5-/1,2,3,4-TeMB values (less than 0.6) (Table 3).

Tricyclic terpenes (TTs) occurs in high abundance with C_{21} and C_{23} homologs being predominant in crude oil indicating a marine (Aquino Neto et al., 1983) and saline lacustrine source (Tao et al., 2015). However, it is often reported that relatively high concentrations of $C_{19}TT$ and $C_{20}TT$ of source rocks and oils are usually related to the contribution of terrestrial organic matter (Peters
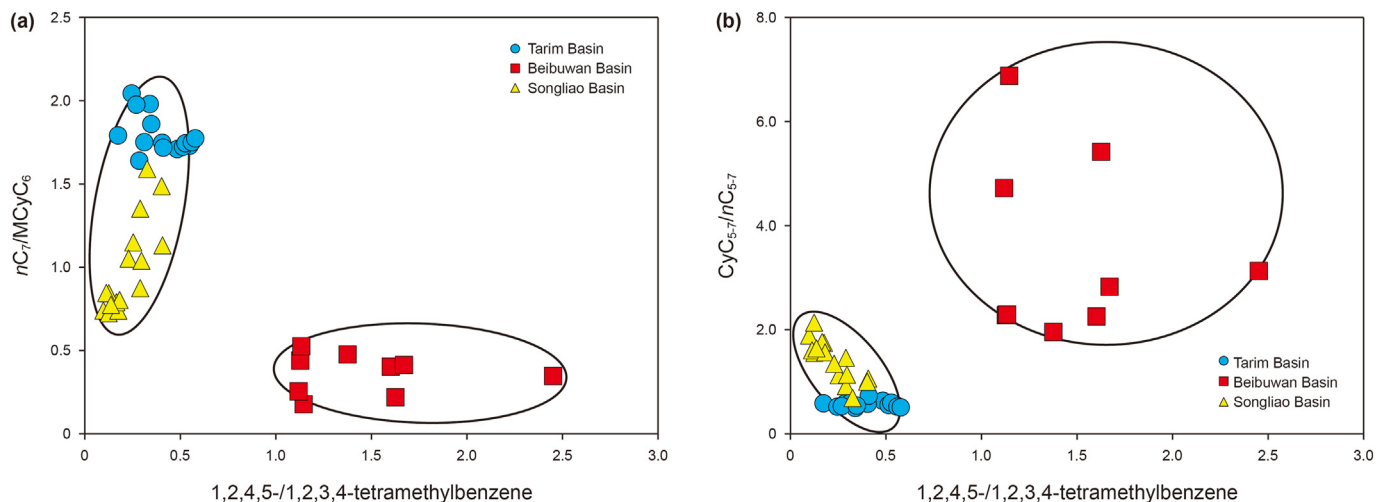
Fig. 8. The cross-plot of 1,2,4,5-/1,2,3,4-tetramethylbenzene vs. (a) $nC_7/MCyC_6$ and (b) CyC_{5-7}/nC_7 for all studied oils. CyC: cycloalkanes, nC_7: n-heptane, $MCyC_6$: methylcyclohexane.
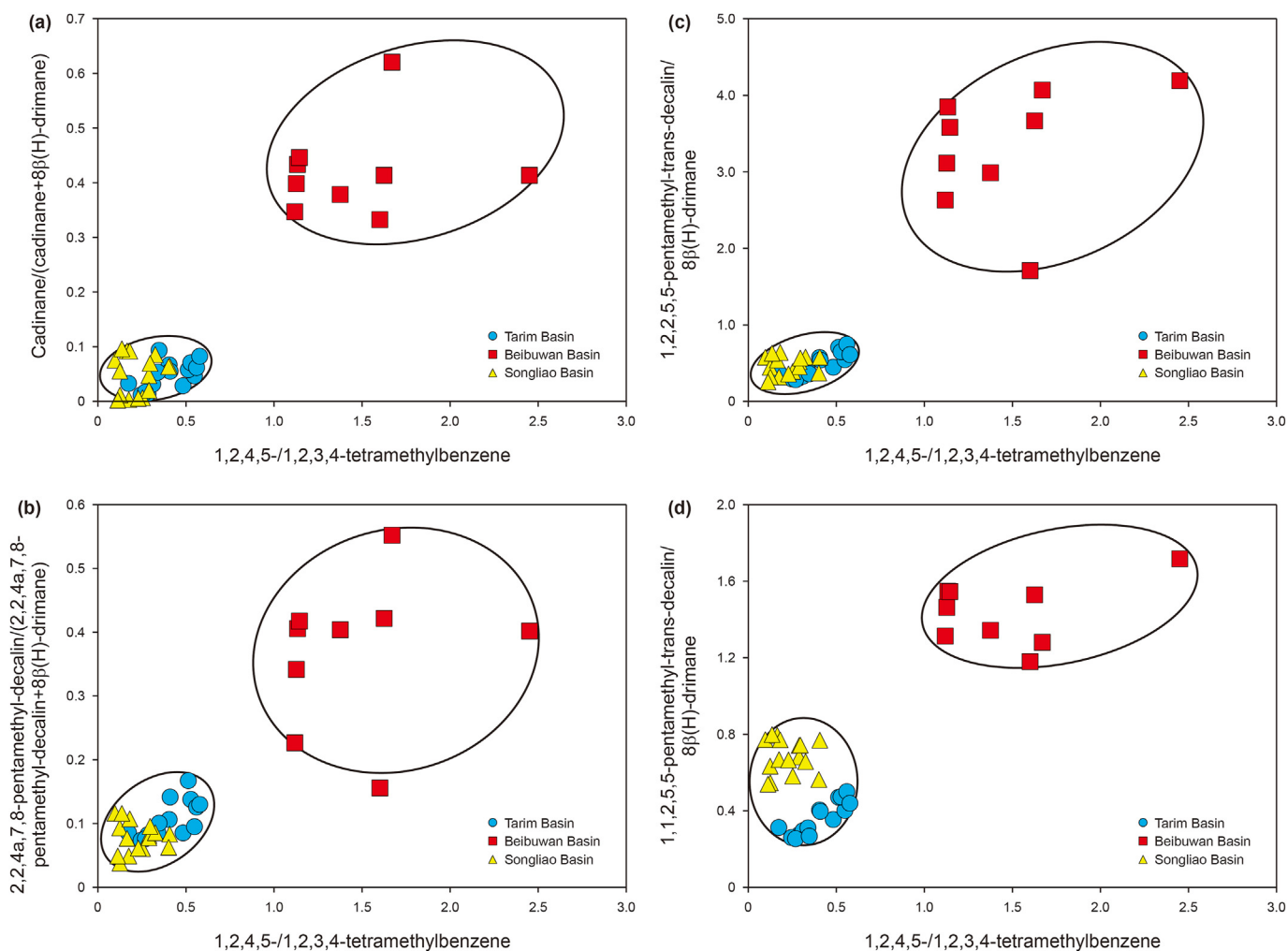
Fig. 9. The cross-plot of 1,2,4,5-/1,2,3,4-tetramethylbenzene vs. (a) cadinane/(cadinane + 8β(H)-drimane), (b) 2,2,4a,7,8-pentamethyl-decalin/(2,2,4a,7,8-pentamethyl-decalin + 8β(H)-drimane), (c) 1,2,2,5,5-pentamethyl-trans-decalin/(1,2,2,5,5-pentamethyl-trans-decalin + 8β(H)-drimane), and (d) 1,1,2,5,5-pentamethyl-trans-decalin/(1,1,2,5,5-pentamethyl-trans-decalin + 8β(H)-drimane) values for all studied oils.

et al., 2005). Oleanane was detected and identified in ancient sediments, indicating a source of angiosperms (Zumberge, 1987). In

Fig. 10, oils derived from the Beibuwan Basin have high $(C_{19}TT + C_{20}TT)/C_{23}TT$ values (2.17—5.69), Oleanane/
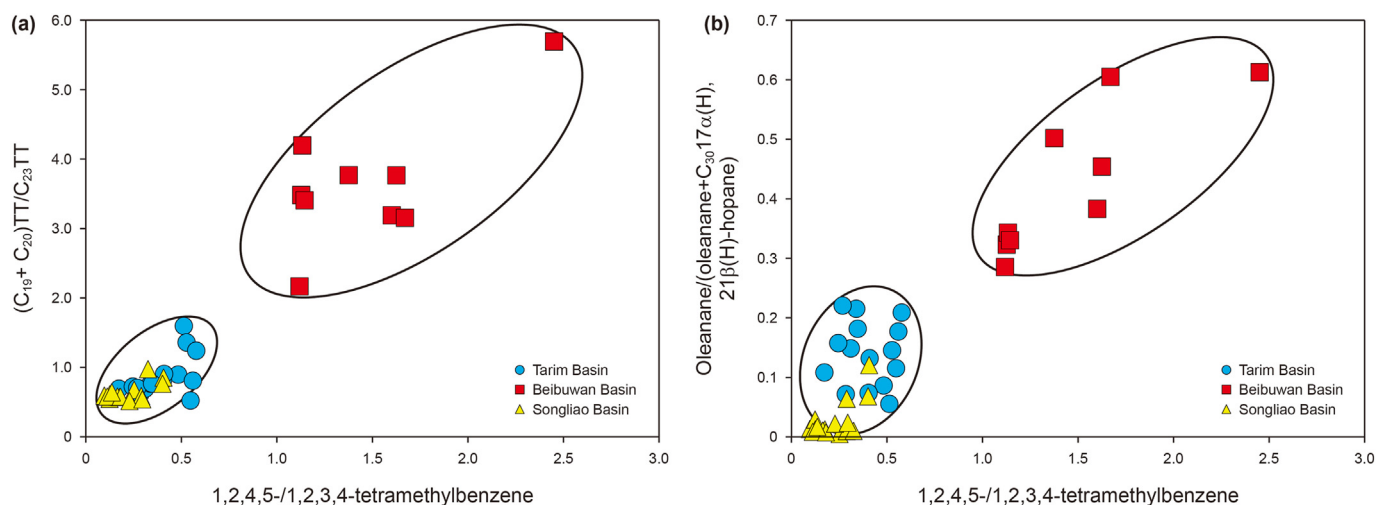
Fig. 10. The cross-plot of 1,2,4,5-/1,2,3,4-tetramethylbenzene vs. (a) ($C_{19}TT + C_{20}TT$)/$C_{23}TT$, and (b) Oleanane/(Oleanane + C_{30} 17α(H), 21β(H)-Hopane) for all studied oils. TT: Tricyclic Terpanes.

(Oleanane + C_{30}17α(H), 21β(H)-Hopane) values (0.29—0.61), and 1,2,4,5-/1,2,3,4-TeMB values (greater than 1.0), whereas oils derived from the Tarim Basin and Songliao Basin have lower ($C_{19}TT + C_{20}TT$)/$C_{23}TT$ values (0.52—1.59 and 0.52—0.98, respectively), Oleanane/(Oleanane + C_{30}17α(H), 21β(H)-Hopane) values (0.06—0.22 and 0—0.12, respectively), and 1,2,4,5-/1,2,3,4-TeMB values (less than 0.6) (Table 3).

In conclusion, oils from the Tarim Basin and Songliao Basin have low 1,2,4,5-/1,2,3,4-TeMB values (less than 0.6) suggesting that oils derived mainly from lower hydrobiont, algae, and bacteria, whereas oils from the Beibuwan Basin have higher 1,2,4,5-/1,2,3,4-TeMB values (greater than 1.0) indicating oils originated mainly from terrestrial higher plants. It should be noted that in terms of distinguishing the source of organic matter, the 1,2,4,5-/1,2,3,4-TeMB parameter cannot distinguish the aquatic species of the Cambrian-Ordovician and Cretaceous periods well compared to the CyC_{5-7}/nC_{5-7}, nC_7/$MCyC_6$, 1,2,2,5,5-pentamethyl-*trans*-decalin/ 8β(H)-drimane and Oleanane/(Oleanane + C_{30}17α(H), 21β(H)-Hopane) parameters. Therefore, compared to organic matter identification, the 1,2,4,5-/1,2,3,4-TeMB parameter is more effective in identifying sedimentary environments.

3.5. Secondary alteration influence on the distribution of 1,2,4,5-TeMB and 1,2,3,4-TeMB in crude oil

Various physical and chemical effects can alter the composition of crude oil, including biodegradation, evaporative fractionation and thermal evolution (Evans et al., 1971; Peters and Fowler, 2002).

3.5.1. Evaporative fractionation

Evaporative fractionation will convert low and intermediate molecular weight hydrocarbons to vapor phase (Thompson, 1987, 1988). To evaluate evaporative fraction, all crude oils were plotted in the commonly used paraffinicity (F, nC_7/$MCyC_6$) versus aromaticity (B, Tol/nC_7) cross-plot of Thompson (1988). Based on experiments and empirical observations, Thompson (1987) proposed that oils that experienced evaporative fraction will deviate from the normal oil with decreasing F ratios (less than 0.5) and increasing B ratios (greater than 1.0). According to the scheme of Thompson (1987), both crude oils from the Tarim Basin (with F values of 1.64—2.09 and B values of 0.08—0.31) and Songliao Basin (with F values of 0.72—1.59 and B values of 0.01—0.10) did not undergone

the effect of evaporative fractionation (Table 3). Besides, oils from the Beibuwan Basin are characterized by higher B values (0.61—2.66) and low F values (0.18—0.53) relative to the Tarim Basin oils and Songliao Basin oils (Table 3). The F values depend on both organic matter source and thermal maturity, and low F values for crude oils from the Beibuwan Basin probably mainly reflect a terrestrial organic matter input. Furthermore, the content of toluene in terrestrial organic matter is usually higher than that of marine organic matter (Leythaeuser et al., 1979a, 1979b). The differences of B values among all studied oils can be observed in Table 3. Additionally, the change of compound into a vapor phase is mainly related to its own vapor pressure that were mainly related to the structure and molecular weight of the compound (Thompson, 1987, 1988). Therefore, the ratio of 1,2,4,5-TeMB to 1,2,3,4-TeMB might not or slightly be affected by evaporative fractionation because 1,2,4,5-TeMB and 1,2,3,4-TeMB have equal molecular weight and analogous molecular skeleton.

3.5.2. Biodegradation

Biodegradation can alter the composition of petroleum, especially in shallow reservoirs. Oils derived from the Beibuwan Basin and Songliao Basin were not detected obvious 25-norhopanes series compounds, indicating these crude oils and condensates did not undergo biodegradation. Although 25-norhopanes were detected in some marine oils from the Tarim Basin, it widely accepted that they remain of palaeobiodegraded petroleum in fresh oils (Chang et al., 2013; Zhang et al., 2014b). In addition, the biodegradation rate of aromatic compounds is inversely proportional to the number of aromatic rings and directly proportional to alkyl substituents (Volkman et al., 1984). Therefore, the 1,2,4,5-TeMB and 1,2,3,4-TeMB may have similar susceptibility to biodegradation. The ratio of 1,2,4,5-TeMB to 1,2,3,4-TeMB may not affect by the biodegradation. The differences of light hydrocarbon composition of the Tarim Basin oils, Songliao Basin oils and Beibuwan Basin oils probably result from their different origins and sedimentary environments.

3.5.3. Thermal maturity

According to the different thermal stability of methyldibenzothiophene (MDBT), ethyldibenzothiophene (EDBT) and dimethyldibenzothiophene (DMDBT) at different substitution positions, 4-MDBT/1-MDBT (MDR), 4-/(4- + 1-MDBT) (MDR'), 4,6-
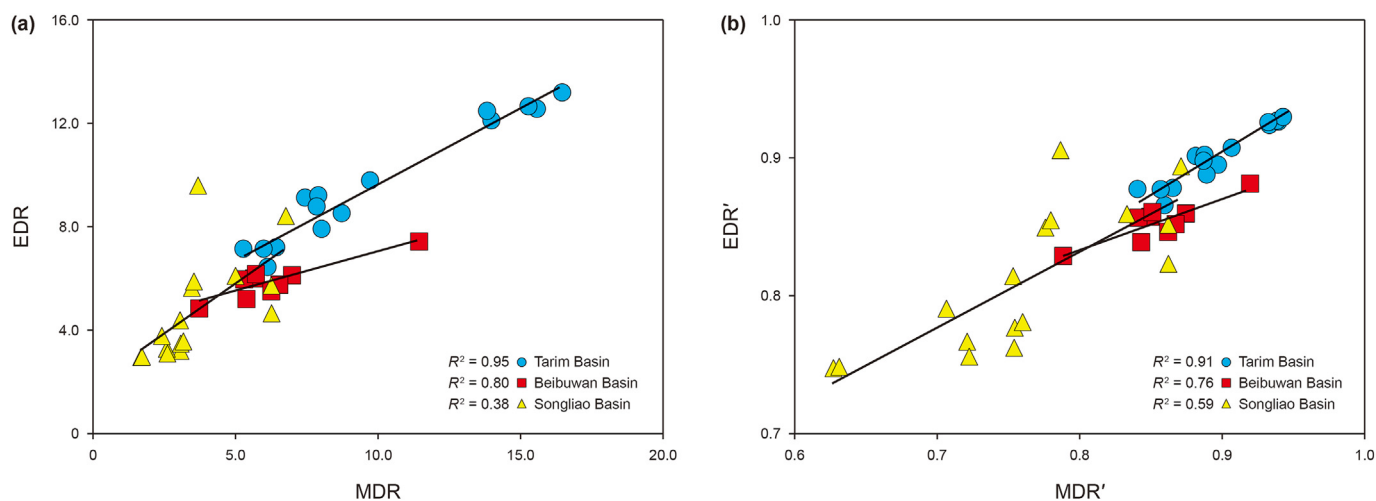
(a)

(b)

Fig. 11. The cross-plot of (a) MDR vs. EDR, and (b) MDR' vs. EDR' for all studied oils.

DMDBT/4-EDBT (EDR) and 4,6-DMDBT/(4,6-DMDBT + 4-EDBT) (EDR') are used to indicate the degree of maturity (Radke and Willsch, 1994; SantamaríA-Orozco et al., 1998). In Fig. 11, the above thermal maturity parameters present a good positive correlation, although the correlation coefficient of the Songliao Basin oils maturity parameters is low. The MDR values of the Tarim Basin oils and the Beibuwan basin oils are in the range of 5.28–16.48 and 3.81–12.05, respectively (Table 3). However, the MDR values of the Songliao Basin oils are in the range of 1.68–6.76, indicating the Songliao Basin oils have lower maturity relative to the Tarim Basin oils and Beibuwan Basin oils (Table 3). MDR', EDR, and EDR' also indicate that the maturity of crude oils from the Beibuwan Basin and the Tarim Basin is higher than that from the Songliao Basin.

Based on the difference in thermal stability of methylphenanthrene (MP) isomers, F1 = [(2-MP + 3-MP)/(2-MP + 3-MP + 1-MP + 9-MP)] and F2 = [2-MP/(2-MP + 3-MP + 1-MP + 9-MP)] are proposed to predict the degree of thermal evolution of crude oil and source rock (Bao et al., 1992). In Fig. 12, the Beibuwan Basin oils and Tarim Basin oils have reached mature to high mature stage, while the Songliao Basin oils has a relatively low degree of thermal evolution. Therefore, the difference of 1,2,4,5-/1,2,3,4-TeMB values in all studied oils are influenced by differing maturity cannot be completely excluded. However, because the Beibuwan Basin oils and Tarim Basin oils have similar maturity range, the difference in 1,2,4,5-/1,2,3,4-TeMB values are not controlled by thermal maturity. 1,2,4,5-/1,2,3,4-TeMB ratio may be used to infer the origin of organic matters and sedimentary environment of ancient sediments.

4. Conclusions

Whole oil samples were examined by GC × GC-TOFMS analysis to reveal the geochemical information contained in the C_0–C_5 alkylbenzenes. With the help of Nist 11.0 and published literatures (Cheng et al., 2015a), a total of 45 alkylbenzenes were identified in crude oils. Quantitative and qualitative data display that the difference in the concentrations of C_6–C_{13} hydrocarbon compounds and total C_0–C_5 alkylbenzenes in the Tarim Basin oils and Beibuwan Basin oils were mainly controlled by the organic matter source and depositional environment of source rocks. However, the lowest C_6–C_{13} hydrocarbon compounds and total C_0–C_5 alkylbenzenes concentrations from the Songliao Basin oils are mainly related to the lower thermal maturity of crude oils. In addition, the differences of total C_0–C_5 alkylbenzenes concentrations in crude oils are
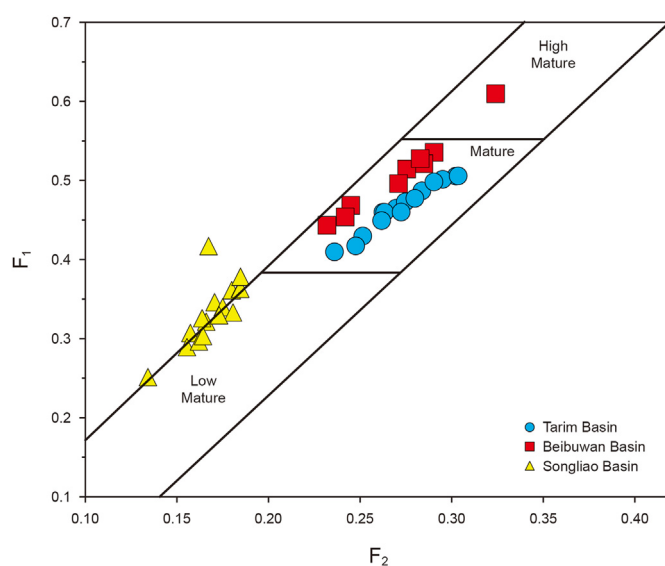

Fig. 12. The cross-plot of F_1 vs. F_2 for all studied oils.

mainly controlled by C_2–C_4 alkylbenzenes contents. Based on depositional environment and organic matter origin, all crude oils can be divided into two groups by 1,2,4,5-/1,2,3,4-TeMB ratio and molecular biomarker parameters. In the present study, oils derived mainly from lower hydrobiont, algae, bacteria and source rocks deposited under reducing/anoxic conditions have low 1,2,4,5-/1,2,3,4-TeMB values (less than 0.6), while oils originated mainly from terrestrial higher plants and source rocks deposited under oxic/sub-oxic conditions have higher 1,2,4,5-/1,2,3,4-TeMB values (greater than 1.0). 1,2,4,5-TeMB content in oils derived from source rocks deposited in oxidized sedimentary environment (greater than 1.0 mg/g whole oil) is higher than that in oils from source rocks deposited in reduced sedimentary environment (less than 1.0 mg/g whole oil). The difference in 1,2,4,5-/1,2,3,4-TeMB values are basically independent of secondary alteration and thermal evolution. Compared with organic matter recognition, the 1,2,4,5-/1,2,3,4-TeMB parameter is more effective in identifying sedimentary environments.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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