Dibenzofuran Series in Terrestrial Source Rocks and Crude Oils and Applications to Oil-Source Rock Correlations in the Kuche Depression of Tarim Basin, NW China*

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Abstract: Ten series of aromatic hydrocarbon compounds (biphenyl, naphthalene, phenanthrene, anthracene, retene, chrysene, benzoanthracene, dibenzofuran, fluorene, dibenzothiophene) isolated from seven Triassic and Jurassic lacustrine mudstone samples and three swamp coal samples, as well as five crude oil samples collected in the Kuche depression of the Tarim Basin, NW China, have been analysed by GC-MS techniques. It is found that the relative abundances of dibenzofuran series are higher in the three swamp coal samples than those in the lacustrine mudstone samples. Based on the similar relative abundances of dibenzofuran series, especially dibenzofuran compound, in the TICs of aromatic hydrocarbons, crude oils from wells SA3 (K), YTK5 (E, K) and QL1 (E) are thought to have been derived predominantly from the coals of the Lower Jurassic Yangxia Formation or Middle Jurassic Kezilenuer Formation, whereas those from wells YM7 (O) and YH1 (E) were derived mainly from Triassic and Jurassic lacustrine mudstones in the Kuche depression. This is the first report about how to distinguish coal-generated oils from lacustrine mudstone-generated oils in the Kuche depression in terms of the dibenzofuran series. The present paper has enlightening and directive significance for further oil-source rock correlations and oil and/or gas exploration in the Kuche depression of the Tarim Basin.

Key words: Tarim Basin; Kuche depression; Triassic; Jurassic; lacustrine mudstone; swamp coal; aromatic hydrocarbon; dibenzofuran; oil-source rock correlation; coal-generated oil; lacustrine mudstone-generated oil

1 Introduction

The Tarim Basin, NW China, is the only basin in China where not only marine, but also terrestrial industrial oil and gas pools are developed. The terrestrial oil and gas pools have been found in the Kuche depression in the northern part of the basin and its front uplift area (Fig. 1). The source rocks of the terrestrial oil and gas pools are Triassic and Jurassic lacustrine mudstones and swamp coals.

The biomarkers from the saturated fractions of Triassic and Jurassic terrestrial source rocks and

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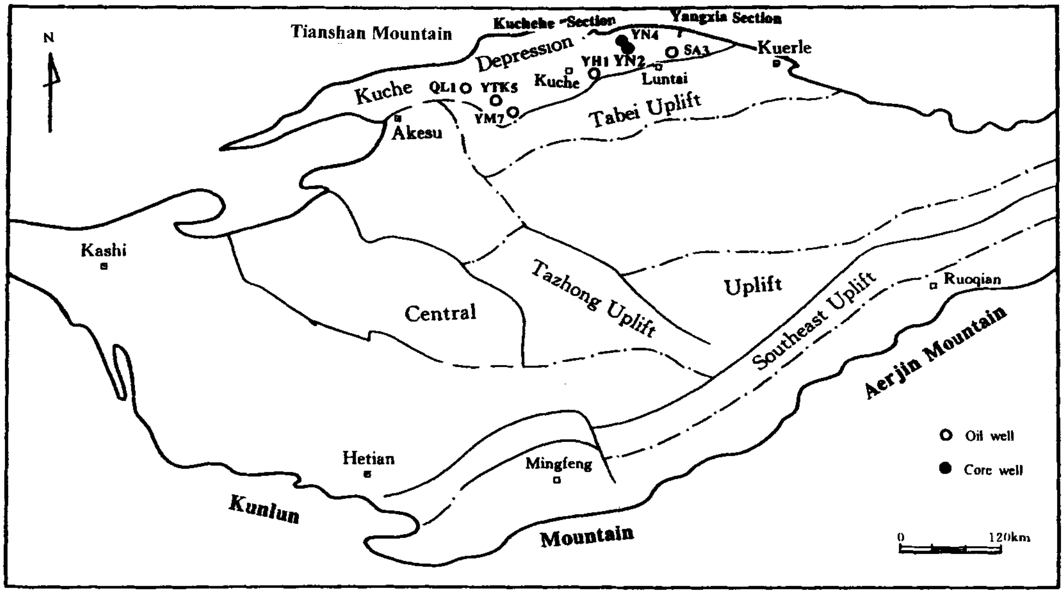

Fig. 1. Location of Triassic and Jurassic terrestrial source rock and crude oil samples in the Kuche depression, Tarim Basin (The map of the Tarim Basin including major structural elements is after Huang Difan and Liang Digang, 1995).

curde oils in the depression were described previously in a number of publications (Liang Digang et al., 1998; Tian Zuoji et al., 2000; Hendix et al., 1995). However, few aromatic compounds have been reported from the Triassic and Jurassic terrestrial source rocks and crude oils in the depression. Aromatic hydrocarbons are ubiquitous in the source rocks and crude oils. They can provide significant information on sedimentary environments, source input, migration, thermal maturity and oil-source correlations (Liu Luofu et al., 1996; Luo Jian et al., 2001; Wei Zhibin et al., 2001). Ten series of aromatic hydrocarbon compounds (biphenyl, naphthalene, phenanthrene, anthracene, retene, chrysene, benzoanthracene, dibenzofuran, fluorene, dibenzothiophene) isolated from the Triassic and Jurassic terrestrial source rocks (lacustrine mudstones and swamp coals) and crude oils in the depression have been analysed in this work. It is found that the relative abundances of naphthalene and biphenyl series in the TICs of aromatic hydrocarbons from the source-rock extracts are commonly low, but generally high in the TICs of aromatic hydrocarbons from crude oil samples; the relative abundances of chrysene series are usually high in the source-rock extracts, whereas generally low in curde oil samples. The anthracene series were detected only in two Middle-Lower Jurassic coal samples, and they are relatively high in abundance. But crude oil samples commonly lack these compounds; the benzoanthracene series have relatively high abundances in three of the coal samples, and are commonly found in lacustrine mudstone samples, although their relative abundances are low. But they are commonly scarce in crude oil samples. The different abundance-changing characteristics of the above aromatic hydrocarbon compounds in the TICs of aromatic hydrocarbons from the source rock and crude oil samples in the Kuche depression are probably due to migration effects. Retenes are present in high abundances in three of the coal samples, but only exist in two lacustrine mudstone samples (KL-01, KL-07) and two oil samples (YH1, YM7), with very low abundances. This is probably attributable to thermal instability of the isopropyl group associated with the retenes. Retenes are readily degraded to 7-ethyl-1-methylphenanthrenes and, to a lesser extent, 1,7-dimethylphenanthrenes with increasing maturity of oil samples (Wilhems et al., 1998), thereafter resulting in the very low abundances or absence of retenes in the curde oil samples; the phenanthrene series are the highest peak groups in the TICs of aromatic hydrocarbons from the most majority of the Triassic and Jurassic mudstone or coal or crude oil samples. Hence, the above aromatic compounds have no substantial geochemical significance for oil-source rock correlations of the Triassic and Jurassic terrestrial source rocks and crude oils in the depression. But the dibenzofuran series are very useful aromatic hydrocarbon compounds in oil-source rock correlations of the Triassic and Jurassic terrestrial source rocks and crude oils. This paper reported different distribution characteristics of dibenzofuran series in the Triassic and Jurassic lacustrine mudstone, swamp coal and crude oil samples collected from the depression, and further provided a new geochemical method to distinguish oils from coals, and those from lacustrine mudstones in the Kuche depression, in terms of the dibenzofuran series, especially dibenzofuran compound.

2 Samples

Seven Triassic and Jurassic lacustrine mudstone and three swamp coal source rock samples were collected from two wells (YN2 and YN4) and two sections (Kuchehe section and Yangxia section) in the Kuche depression, respectively (Fig. 1, Table 1). The TOC values for the seven lacustrine mudstone samples range from 0.22% to 14.38%, with an average value of 3.38% and their R_o values vary from 0.66% to 1.16%, indicating a moderate maturity; the TOC values for the three coal samples are 80% or so and the R_o values are within the range of 0.6% – 0.7%, putting them at the marginally mature stage. All of the basic geological and geochemical data for the source rock samples studied from the Kuche depression are summarized in Table 1.

Table 1. Basic geological and geochemical data for the Triassic and Jurassic source rock samples from the Kuche depression, Tarim Basin

Type	Sample No.	Well No.	Depth (m)	Lithology	Age(1) and formation(2)	TOC(3) (%)	R_o(3) (%)	DBF(4)/MDBF	MDBF(5)/DMDBF	DBF(6)/The highest peak
Lacustrine mudstone	KL-01	YN2	4800	Greyish black mudstone	J_1a	0.22	1.13	-	1.09	- (DBF/CH)
	KL-02	YN2	4403	Black mudstone	J_1y	3.72	1.02	0.34	1.78	0.016 (DBF/P)
	KL-03	YN2	5003	Black mudstone	T_3t	1.15	0.96	-	1.08	- (DBF/P)
	KL-04	YN2	5245	Black mudstone	T_3h	0.68	1.16	-	-	- (DBF/2-MP)
	KL-07	YN4	3996	Black mudstone	J_1a	3.20	0.83	0.35	1.18	0.024 (DBF/P)
	KL-08	YN4	4630	Black mudstone	J_1a	0.31	0.86	0.19	1.15	0.008 (DBF/P)
	KC-5	Kuchehe section	Outcrop	Black carbonaceous mudstone	J_2q	14.38	0.66	-	1.05	- (DBF/P)
Swamp coal	KL-05	YN2	4317	coal	J_2kz	77.32	0.68	0.32	1.61	0.036 (DBF/P)
	Y3	Yangxia section	coal mine	coal	T_3t	82.45	0.59	0.59	1.86	0.138 (DBF/P)
	Y5	Yangxia section	coal mine	coal	J_1y	80.11	0.64	0.27	1.00	0.041 (DBF/P)

(1) J_1. Lower Jurassic; J_2. Middle Jurassic; T_3. Upper Triassic. (2) a. Ahe Formation; y. Yangxia Formation; h. Huangshangjie Formation; q. Qiakemake Formation; kz. Kezilenuer Formation; t. Taliqike Formation. (3) The TOC and R_o data for these rocks were determined at the Research Institute of Petroleum Exploration and Development (RIPED), PetroChina in Beijing. (4) The ratios of DBF/MDBF and (5) those of MDBF/DMDBF were calculated based on peak heights in the mass chromatograms of their multiple ion detection at m/z168, m/z182 and m/z196. DBF. dibenzofuran; MDBF. methyldibenzofuran; DMDBF. dimethyldibenzofuran. (6) The ratios of DBF/the highest peak were calculated based on peak heights in their TICs of aromatic hydrocarbons, indicating the relative abundances of dibenzofurans in different types of source rocks and crude oils. CH. chrysene; P. phenanthrene; 2-MP. 2-methylphenanthrene.

Five terrestrial crude oil samples were collected from five wells (YH1, YTK5, SA3, YM7 and QL1) (Fig. 1). The basic geological and geochemical data for these oil samples are summarized in Table 2.

Table 2. Basic geological and geochemical data for the terrestrial crude oil samples studied in the Kuche depression

Sample No.	Well No.	Depth (m)	Res. age(1)	$\delta^{13}C$ (‰)(2)	DBF(3)/MDBF	MDBF(4)/DMDBF	DBF(5)/The highest peak
Tm-23	YH1	5451 - 5466	E	-29.4	-	0.33	- (DBF/P)
Tm-25	YTK5	5310 - 5315, 5332 - 5334	E, K	-28.3	0.67	1.18	0.036 (DBF/P)
Tm-30	SA3	5047 - 5051	K	-26.0	0.79	0.88	0.048 (DBF/P)
Tm-31	YM7	5597 - 5607, 5616 - 5621	O	-29.8	-	0.56	- (DBF/P)
Tm-32	QL1	5759.1 - 5769.89	E	-28.2	1.75	1.33	0.048 (DBF/BP)

(1) E. Lower Tertiary; K. Cretaceous; O. Ordovician. (2) The data of $\delta^{13}C$(‰) for the crude oil samples were determined at the Key Laboratory of Gas Geochemistry, Lanzhou Institute of Geology, Chinese Academy of Sciences, Lanzhou. (3) - (5) The ratios in the crude oil samples were calculated with the same method as in the calculation of ratios for (4), (5) and (6) in Table 1.

3 Experimental

Whole-rock samples were ground as fine as 100 mesh after surface cleaning, and subsequently extracted for 72 hours at 70℃ with chloroform. After the removal of asphaltenes, both extracts and oil samples were fractionated by silica-alumina column chromatography. The saturate fractions were eluted with hexane, aromatics with dichloromethane, and polars with methanol. The aromatic fractions were concentrated and analyzed by GC-MS in both multiple ion detection (MID) and full scan modes. An HP 5973 mass spectrometer was coupled to a HP 6890 GC and equipped with a 30 m (0.25 mm i.d., 0.33 μm film thickness) SE-54 column for GC-MS analysis. The oven temperature was programmed from 60℃ to 160℃ (at 5℃ min^{-1}), then to 270℃ (at 2℃ min^{-1}) and held for 10 min at 160℃ and for 20 min at 270℃. The carrier gas was helium with a flow rate of 0.2 ml · min^{-1}; ion source temperature 230℃; injector temperature 250℃; transfer-line temperature 280℃; electron emission 34.6 μA; electron energy 70 eV. The ions used for tentative identification and monitoring the aromatic hydrocarbons are listed in Table 3.

4 Results and discussion

It has been reported that variations in relative abundances of fluorenes, dibenzofurans and dibenzothiophenes may serve as a good indicator of sedimentrary environments of source rocks. The concentrations of dibenzothiophene series are high in marine carbonate source rocks, whereas those of fluorene and dibenzofuran series are high in freshwater source rocks (Fan Pu et al., 1990). Therefore the fluorene, dibenzofuran and dibenzothiophene series can be further used in oil-source rock correlation study. Results presented in this paper show that no difference is noticed in distribution of fluorene series in the Triassic and Jurassic lacustrine mudstone and coal samples in the Kuche depression. The composition distribution patterns of fluorene series in the lacustrine mudstone and coal samples studied all are of methylfluorene, dimethylfluorene and trimethylfluorene type (fluorene coelutes with the last isomer of trimethylnaphthalene, and the first isomer of dimethylbiphenyl). In addition, the relative abundances of fluorene series in the TICs of aromatic hydrocarbons extracted from lacustrine mudstone samples also are similar to those of coal samples. The distributions of dibenzothiophene series in the TICs of aromatic hydrocarbons from Triassic and Jurassic lacustrine mudstone and coal samples in the Kuche depression also make no difference. The composition distribution patterns of dibenzothiophene series in the TICs of aromatic hydrocarbons from the lacustrine mudstone and swamp coal samples all are of *dibenzothiophene*, *methyldibenzothiophene* type (very low concentrations of dimethyldibenzothiophenes are overshadowed by relatively high concentrations of trimethylfluorenes). Furthermore their relative abundances in the TICs of aromatic hydrocarbons from the lacustrine and swamp coal samples are very low. Hence, they are the same as those aromatic hydrocarbon compounds mentioned above in the section of "Introduction" (naphthalene, biphenyl, chrysene, anthracene, benzoanthracene, retene, phenanthrene series), and the fluorene and dibenzothiophene series are of no actual geochemical significance for oil-source rock correlations of Triassic and Jurassic terrestrial source rocks and crude oils in the Kuche depression. But our deep-going study shows that the distributions of dibenzofuran series in the Triassic and Jurassic lacustrine mudstone, coal and crude oil samples studied in the Kuche depression make a great difference. The dibenzofuran series compounds are very useful aromatic hydrocarbon compounds for the purpose of undertaking oil-source rock correlations between Triassic and Jurassic terrestrial source rocks and crude oils in the Kuche depression.

Table 3. Identification of the aromatic hydrocarbons studied

Series	m/z	Homolog	Skeleton *
BP	154, 168, 182, 196	BP, MBP, DMBP, TMBP	I
N	128, 142, 156, 170, 184	N, MN, DMN, TMN, TeMN	II
DBF	168, 182, 196	DBF, MDBF DMDBF	III
F	166, 180, 194, 208	F, MF, DMF, TMF	IV
DBT	184, 198, 212, 226, 240	DBT, MDBT, DMDBT, TMDBT, TeMDBT	V
P	178, 192, 206, 220, 234	P, MP, DMP, TMP, TeMP	VI
AN	178, 192, 206, 220, 234	AN, MAN, DMAN, TMAN, TeMAN	VII
RE	234	RE	VIII
CH	228, 242, 256, 270	CH, MCH, DMCH, TMCH	IX
BAN	228, 242, 256, 270	BAN, MBAN, DMBAN, TMBAN	X

* Structures shown in the Appendix. BP. biphenyl; N. naphthalene; DBF. dibenzofuran; F. fluorine; DBT. dibenzothiophene; P. phenanthrene; An. anthrancene; RE. retene; CH. chrysene; BAN. benzoanthracene.

4.1 Distribution characteristics of dibenzofuran series from Triassic and Jurassic terrestrial source rocks in the Kuche depression

During detecting methyl-, dimethyl- and trimethylbiphenyls, the dibenzofuran series (dibenzofurans, methyl- and dimethyldibenzofurans among which, methyldibenzofurans have the highest relative abundances, the dibenzofurans possess the lowest relative abundances) were found in seven Triassic and Jurassic lacustrine mudstone and three coal samples in the Kuche depression.

The methyl- and dimethyldibenzofurans commonly exist in the TICs of aromatic hydrocarbons from the seven Triassic and Jurassic lacustrine mudstone samples studied, with the exception of KL-04 sample (methyldibenzofurans coelute with various tetramethylnaphthalene isomers; the first dimethyldibenzofuran isomers coelute with the last tetramethylnaphthalene isomers). The relative abundance and isomer composition of these methyl- and dimethyldibenzofurans, especially methyldibenzofurans in the TICs of aromatic hydrocarbons are exceedingly consistent with those in m/z182 methyldibenzofuran mass chromatograms of these lacustrine mudstone samples. In addition, dibenzofurans

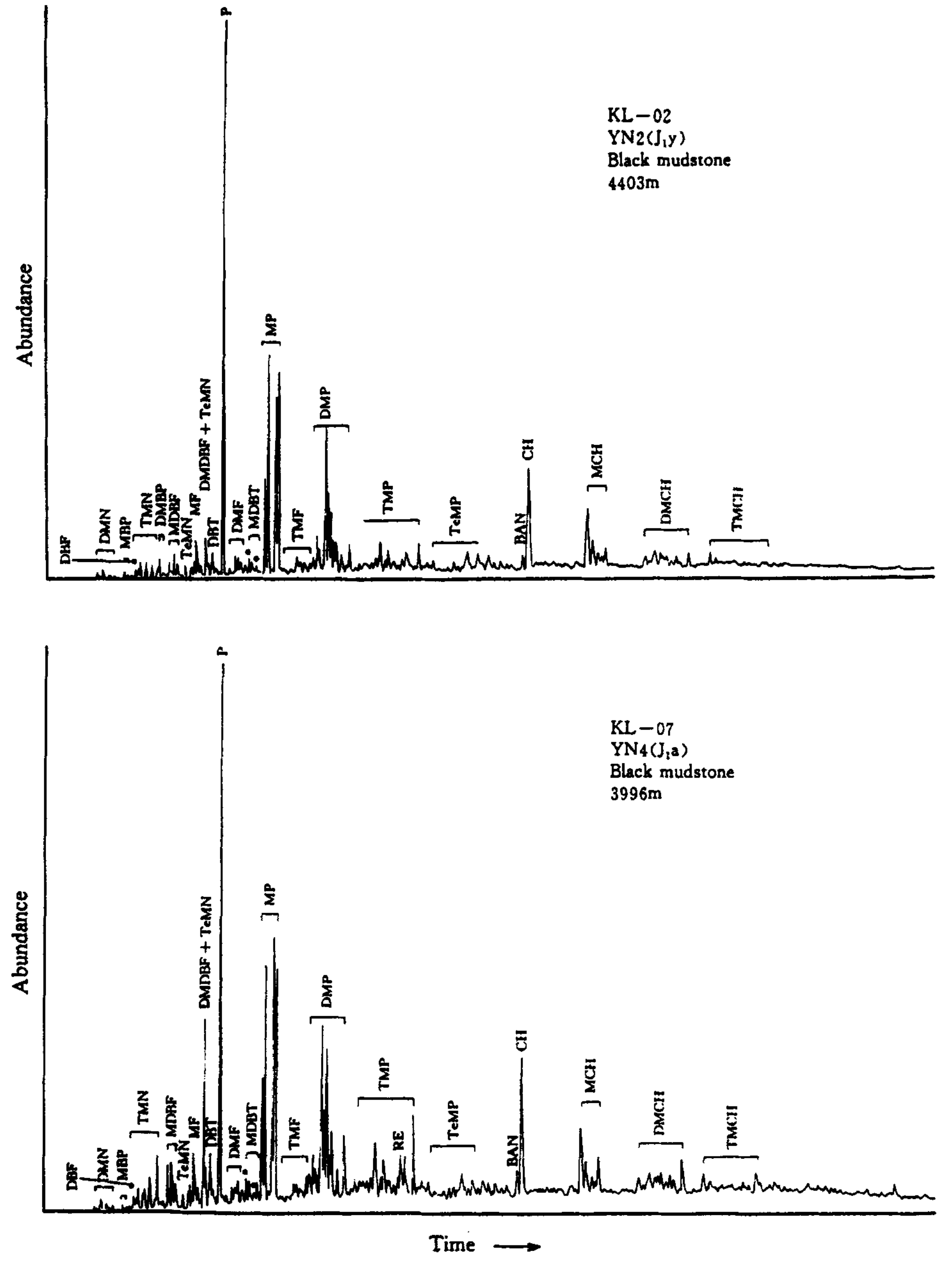

Fig. 2. TICs of aromatic hydrocarbons from some Lower Jurassic lacustrine mudstone samples in the Kuche depression, with very low abundances of dibenzofurans (DBF = dibenzofuran).

are present in relatively low abundances as observed in TIC chromatograms of the aromatic hydrocarbons for the three Lower Jurassic mudstone samples (KL-02, YN2, 4403 m, J_1y; KL-07, YN4, 3996 m, J_1a; KL-08, YN4, 4630 m, J_1a) (the ratios of DBF/the highest peak are 0.016, 0.024 and 0.008, respectively; Table 1), which have relatively high abundances of methyl- and dimethyl-

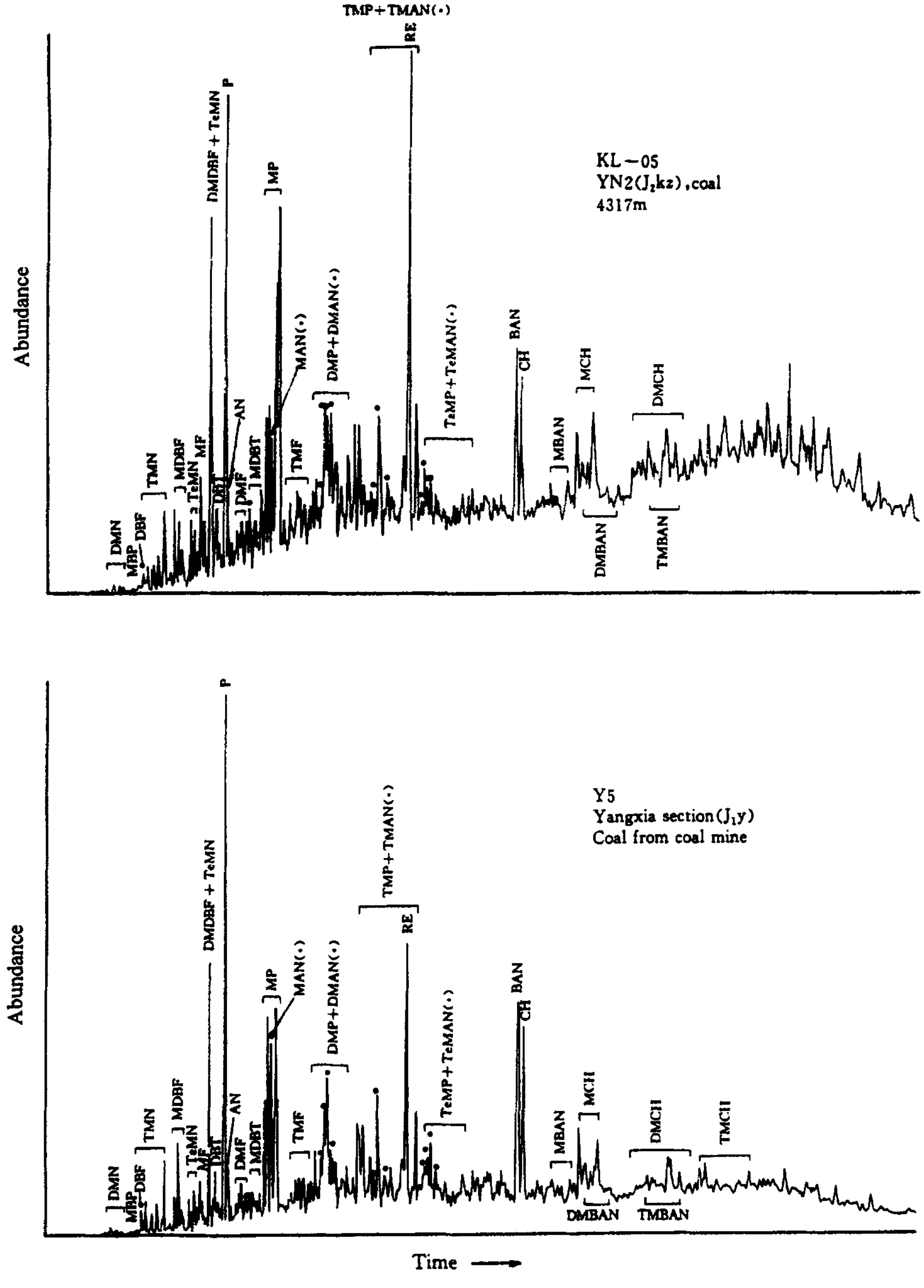

Fig. 3. TICs of aromatic hydrocarbons from Middle-Lower Jurassic coal samples in the Kuche depression, with relatively high abundances of dibenzofurans (DBF = dibenzofuran).

dibenzofurans (dibenzofuran elutes between the first two isomers of trimethylnaphthalene) (Fig. 2). In comparison, the relative abundances of methyl- and dimethyldibenzofurans in the TICs of ar-

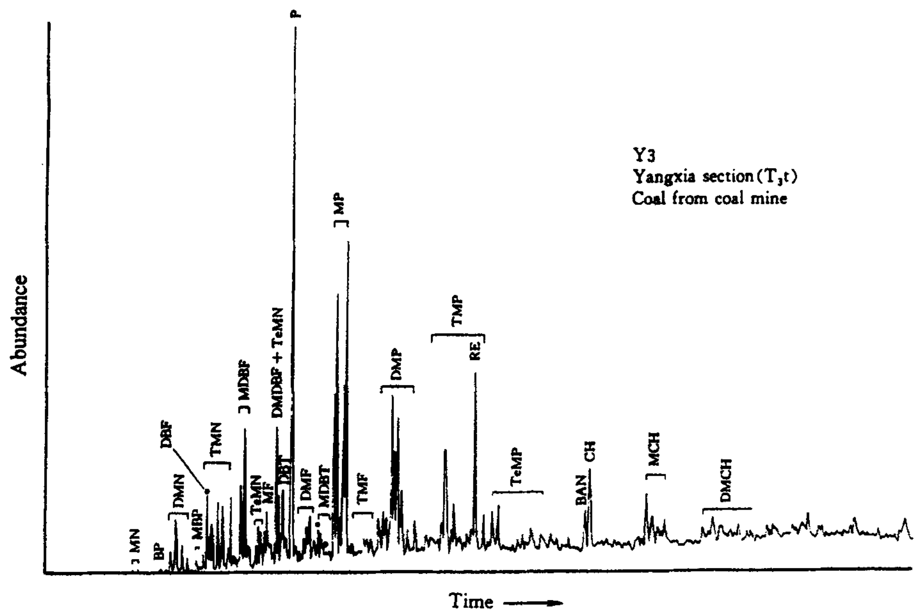

Fig. 4. TICs of aromatic hydrocarbons from an Upper Triassic coal sample in the Kuche depression, with high abundances of dibenzofurans (DBF = dibenzofuran).

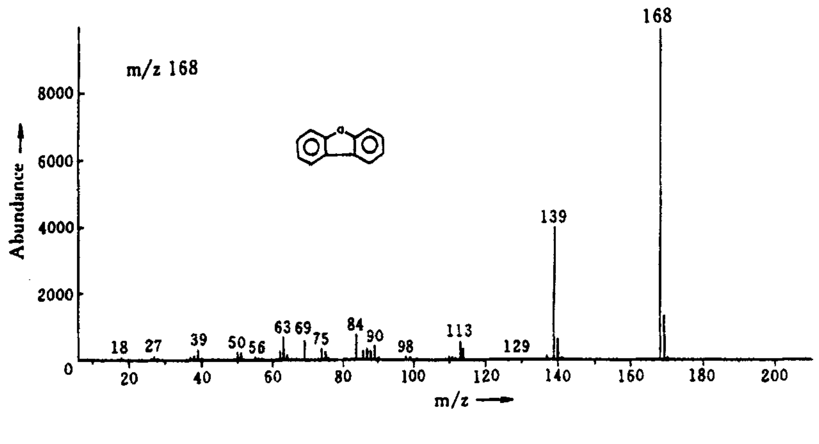

Fig. 5. Mass spectrum of dibenzofuran compounds in the Upper Triassic coal sample (Y3) from the Kuche depression.

omatic hydrocarbons from the three Triassic and Jurassic coal samples in the Kuche depression are much higher than those of the lacustrine mudstone samples. Meanwhile, the abundances of dibenzofurans are higher in these coal samples (the ratios of DBF/the highest peak are 0.036, 0.138 and 0.041, respectively; Table 1, Figs. 3 and 4; mass spectrum of dibenzofuran is in Fig. 5) than those in the three Lower Jurassic lacustrine mudstone samples (Table 1, Fig. 2). The relatively high abundances of dibenzofuran series in the coal samples suggest that the swamp environment is most advantageous to the formation of the dibenzofuran series. It is found that the relative abundance of dibenzofuran series in the Triassic coal sample (Y3) (Fig. 4) is much higher than that in the two Middle and Lower Jurassic coal samples (KL-05, J_2kz; Y5, J_1y) (Fig. 3). This is probably attrib-

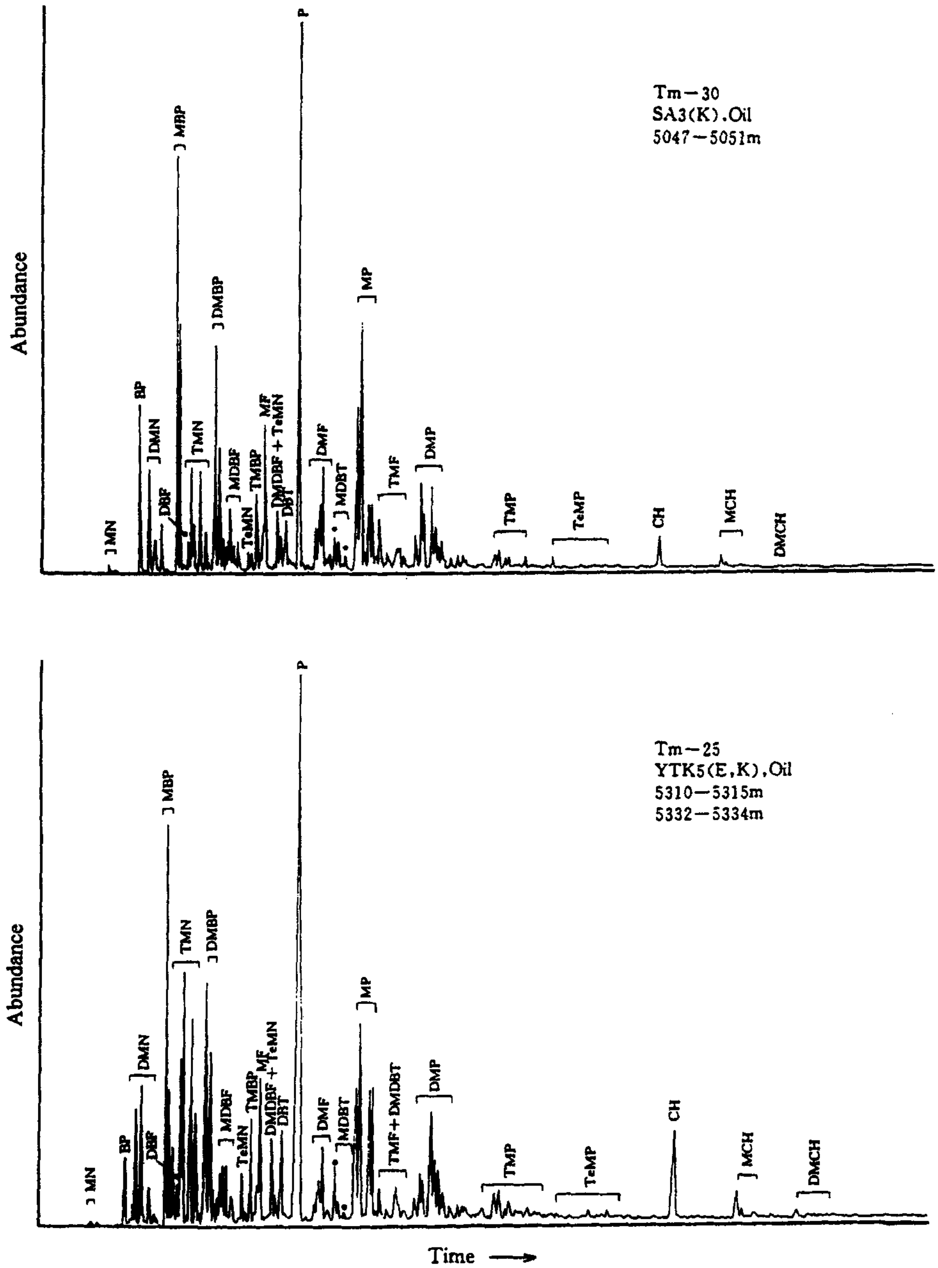

Fig. 6. TICs of aromatic hydrocarbons from well SA3 (K) and well YTK5 (E, K) crude oil samples, with relatively high abundances of dibenzofurans, similar to those in the Lower-Middle Jurassic coal samples from the Kuche depression.

utable to certain differences in redox conditions under which the Upper Triassic and Middle-Lower Jurassic coals were formed.

4.2 Distribution characteristics of dibenzofuran series in Triassic and Jurassic terrestrial crude oils in the Kuche depression and oil-source rock correlations

Methyl- and dimethyldibenzofurans are commonly present in the TICs of aromatic hydrocarbons from the five terrestrial crude oil samples in the Kuche depression. The relative abundances of these methyl- and dimethyldibenzofurans are similar to those of the Triassic and Jurassic mudstone and coal samples from the depression. In addition, higher abundances of dibenzofurans were observed in the TICs of aromatic hydrocarbons from the three terrestrial crude oil samples (YTK5, SA3, QL1) (Fig. 6). The relative abundances of dibenzofurans in the three oil samples (the ratios of DBF/the highest peak are 0.063, 0.048 and 0.048, respectively; Table 2) are considerably higher than those in the TICs of aromatic hydrocarbons from the above three Lower Jurassic lacustrine mudstone samples (KL-02, J_1y; KL-07, J_1a; KL-08, J_1a) containing dibenzofurans (the ratios in the three mudstone samples are 0.016, 0.024 and 0.008; Table 1) (Fig. 2). However, the relative abundances of dibenzofurans from the three oil samples are considerably lower than those of the Upper Triassic coal sample (Y3) (the ratio for Y3 sample is 0.138, Table 1) (Fig. 4). The relative abundances of dibenzofurans in the three oil samples are similar to those in the two Jurassic coal samples (Y5, J_1y; KL-05, J_2kz) (the ratios for the two coal samples are 0.041 and 0.036, Table 1, Fig. 3). Hence it is extrapolated that the three terrestrial crude oil samples were probably derived from coals of the Lower Jurassic Yangxia Formation or Middle Jurassic Kezilenuer Formation in the Kuche depression. The other two oil samples (YH1, YM7) were probably derived from Triassic and Jurassic lacustrine mudstones in the Kuche depression because of very low abundances of methyl- and dimethyldibenzofurans (without dibenzofurans) in the TICs of aromatic hydrocarbons from other three Triassic and Jurassic lacustrine mudstone samples (KL-01, YN2, J_1a; KL-03, YN2, T_3t; KC-5, Kuchehe section, J_2q; Table 1), very similar to the distribution characteristics of dibenzofuran series in the two oil samples (YH1 and YM7; Table 2).

5 Conclusions

(1) Relative abundances of dibenzofuran series in the Triassic and Jurassic swamp coal extracts are higher than those in the Triassic and Jurassic lacustrine mudstone extracts.

(2) Based on the relative abundances of dibenzofuran series, especially dibenzofuran compounds, in rock and oil samples, well SA3 (K), well YTK5 (E, K) and well QL1 (E) crude oils are probably derived from coals of the Lower Jurassic Yangxia Formation or Middle Jurassic Kezilenuer Formation in the Kuche depression. Well YM7 (O) and well YH1 (E) crude oils are probably derived from Triassic and Jurassic lacustrine mudstones of the depression.

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Appendix