

Qualitative and Quantitative Analysis of Dibenzofuran, Alkyldibenzofurans, and Benzo[*b*]naphthofurans in Crude Oils and Source Rock Extracts

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ABSTRACT: Dibenzofuran (DBF), its alkylated homologues, and benzo[*b*]naphthofurans (BNFs) are common oxygen-heterocyclic aromatic compounds in crude oils and source rock extracts. A series of positional isomers of alkyldibenzofuran and benzo[*b*]naphthofuran were identified in mass chromatograms by comparison with internal standards and standard retention indices. The response factors of dibenzofuran in relation to internal standards were obtained by gas chromatography–mass spectrometry analyses of a set of mixed solutions with different concentration ratios. Perdeuterated dibenzofuran and dibenzothiophene are optimal internal standards for quantitative analyses of furan compounds in crude oils and source rock extracts. The average concentration of the total DBFs in oils derived from siliciclastic lacustrine rock extracts from the Beibuwan Basin, South China Sea, was 518 $\mu\text{g/g}$, which is about 5 times that observed in the oils from carbonate source rocks in the Tarim Basin, Northwest China. The BNFs occur ubiquitously in source rock extracts and related oils of various origins. The results of this work suggest that the relative abundance of benzo[*b*]naphthofuran isomers, that is, the benzo[*b*]naphtho[2,1-*d*]furan/{benzo[*b*]naphtho[2,1-*d*]furan + benzo[*b*]naphtho[1,2-*d*]furan} ratio, may be a potential molecular geochemical parameter to indicate oil migration pathways and distances.

INTRODUCTION

Dibenzofuran (DBF), its alkylated homologues, and benzo[*b*]naphthofurans (BNFs) (Figure 1) are important oxygen-heterocyclic aromatic compounds in oils, coals, sediment extracts, and tar deposits. The presence of DBF in bituminous coals has been recognized.¹ Dibenzofuran is one of the most ecotoxic heterocyclics (HETs).² Because of their comparatively high aqueous solubilities, low octanol–water partition coefficients, high toxicities, and relatively long and persistent plumes, a number of key HETs, including dibenzofuran, methyl dibenzofurans, and dimethyl dibenzofurans, are recommended for the assessment of coal-tar-contaminated aquifers.² Dibenzofuran and benzo[*b*]naphtho[2,3-*d*]furan (BN23F) can react with chlorine atoms to yield polychlorinated dibenzofurans (PCDFs) during the combustion of municipal solid waste in incinerators.³ DBF and other heterocyclic aromatic compounds are also observed in combustion flue gases of lignite,³ which can cause environmental problems.⁴

Dibenzofuran and its alkylated homologues (collectively abbreviated as DBFs) and benzo[*b*]naphthofurans have also been applied as important molecular markers in organic geochemistry. The occurrence and distribution of DBFs are mainly dependent on the source rock type and/or depositional environment.^{5–7} DBFs seem to prevail in freshwater source rocks, terrestrial oils, and coals,^{5,6,8–10} whereas their sulfur-heterocyclic counterparts dibenzothiophenes (DBTs) are more abundant in marine shales and carbonates.^{10–12} The relative abundance of alkyldibenzothiophene (ADBT) with respect to alkyldibenzofuran (ADBF) has been proposed to distinguish depositional environments.^{7,13,14} More recently, researchers also observed that the absolute concentrations of DBFs in petroleum are also affected by

secondary migration processes.⁹ Thus, the DBFs in petroleum are potential molecular indices to indicate petroleum migration distances and filling pathways.⁹

Four methyl dibenzofuran isomers (MDBFs), i.e., 4-, 2-, 3-, and 1-MDBF, were identified by coinjection of internal standards in gas chromatography–mass spectrometry (GC–MS) analyses of aromatic fractions of crude oils and rock extracts.⁷ The standard retention indices for seven dimethyl dibenzofuran (DMDBF) isomers have also been reported.¹⁵ A total of 11 peaks were observed in the *m/z* 196 mass chromatograms that potentially correspond to nine DMDBF and two ethyldibenzofuran (EDBF) isomers.¹⁵ However, the specific molecular structures, i.e., the positions of the ethyl group or the two methyl groups for each isomer and the distribution patterns of DMDBF isomers in crude oils and rock extracts have not yet been reported.

The origin of DBFs in oil and sedimentary organic matter remains a controversial issue. Previous studies suggest that DBFs may originate from dehydrated and condensed polysaccharides^{13,17} or from the oxidative coupling of phenols.¹⁸ High abundances of DBF, DBT, and biphenyl in Permian rocks (East Greenland) probably derived from phenolic compounds of lignin of the woody plants.¹⁹ The majority of natural products related to dibenzofuran are metabolites of lichens or higher fungi. The lichen dibenzofurans appear to be formed by carbon–carbon oxidative coupling of orsellinic acid and its homologues.²⁰ Thus, in 2000 Radke et al.⁷ proposed that DBFs in crude oil

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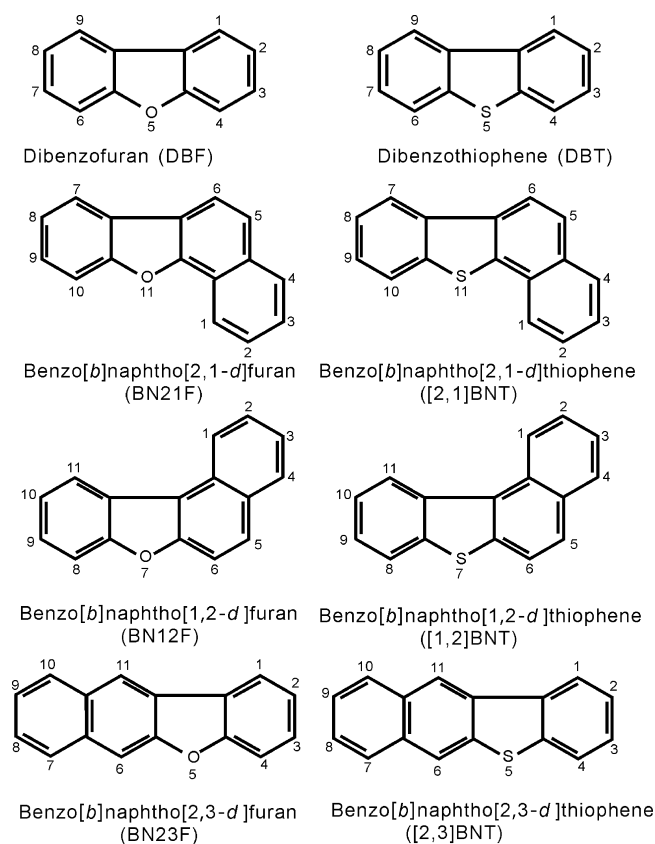


Figure 1. Comparison of the structures of dibenzofuran, dibenzothiophene, benzo[*b*]naphthofurans, and benzo[*b*]naphthothiophenes discussed in the text.

and sediment extracts are potential biomarkers for lichens. However, further work is needed to confirm the precursor–product relationship between lichens and DBFs.

Simulation experiments and geological observations showed that biphenyl and oxygen can form dibenzofuran.²¹ Similarly, methyl-substituted biphenyls can react to yield the corresponding methylated DBFs. The derivatives of biphenyl are commonly used as reactants to synthesize dibenzofurans in the laboratory.²⁰ More geological evidence and laboratory experiments are still needed to fully understand the origin and evolution of DBFs in the geosphere.

Quantifications of DBFs in oils and rock extracts are typically carried out by comparison of peak areas in mass chromatograms of selected ions in GC–MS with those of authentic standards. The commonly used internal standards in previous studies were squalane,²² 1,1'-binaphthyl,²³ and 1- and 2-phenylnaphthalene.⁷ Some perdeuterated aromatic compounds, e.g., phenanthrene-*d*₁₀²¹ and dibenzothiophene-*d*₈,²⁴ are also common internal standards for quantitative analyses of DBFs, PAHs, and DBTs.

The use of internal standards can yield more accurate results compared with the external approach. The best internal standards are chemically similar to the target compound because any loss of the target compound during the experimental procedure is replicated by the loss of internal standard, making this a self-correcting system.²⁵ Isotopically labeled versions of the target compounds are ideally suited for this purpose, and deuterated dibenzofuran (DBF-*d*₈) is the compound of choice as an internal standard for quantitative analysis of DBFs in crude oils and rock extracts.

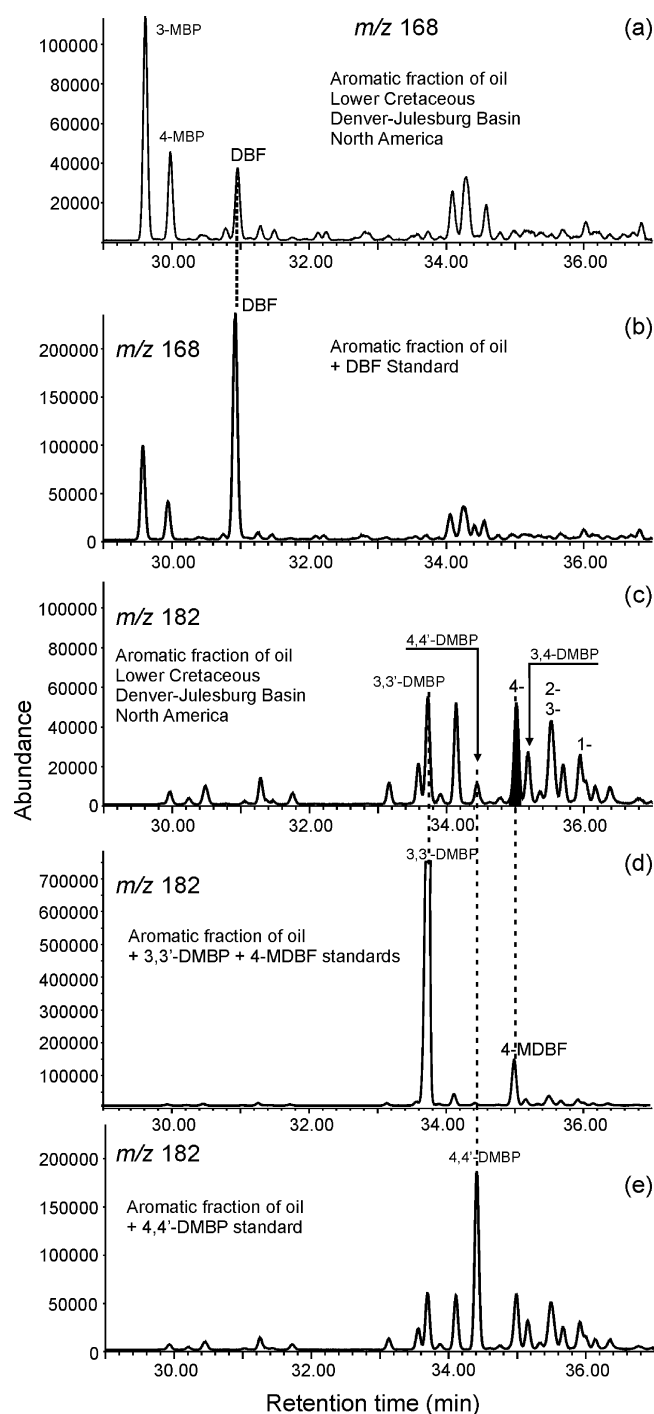


Figure 2. Mass chromatograms for the identification of dibenzofuran and methylated dibenzofuran in an oil sample. MBP, methylbiphenyl; DMBP, dimethylbiphenyl; DBF, dibenzofuran; MDBF, methylated dibenzofuran. Numbers on peaks indicate the methyl substitution pattern on DBFs.

In this paper, we report the DBF, MDBFs, DMBFs, EDBFs, and BNFs identified in crude oils and rock extracts by comparison with coinjected internal standards in GC–MS analyses and correlation with standard retention indices reported in the literature. Furthermore, we report the response factors of DBFs and BNFs to deuterium-labeled internal standards DBF and DBT in GC–MS analyses. We also compare the distribution patterns of BNFs in source rocks and oils derived from typical marine carbonate, marine shale, lacustrine shale, and fluvial/deltaic source facies.

Table 1. Comparison of Calculated Retention Indices for MDBFs in Oils, Coal, and Sedimentary Rock Extracts with Those in the Literature^a

compound	I_{ref}^b	oil, Cretaceous, marine shale, Denver–Julesburg Basin, North America		oil, well H10, Tertiary, lacustrine shale, Beibuwan Basin, South China Sea		oil, Ordovician, marine carbonate, Tarim Basin, NW China		rock extracts, Tertiary, lacustrine shale, Liaohé Basin, East China		identification
		t_R	I	t_R	I	t_R	I	t_R	I	
naphthalene	200.00	17.338	200.00	17.932	200.00	18.138	200.00	18.637	200.00	naphthalene
DBF	258.77	30.956	257.84	31.657	258.01	31.797	258.75	32.399	257.89	DBF
MDBF	273.41									
MDBF	275.04	35.016	275.08	35.711	275.14	35.844	275.03	36.450	274.93	4-MDBF
MDBF	276.15	35.528	277.25	36.210	277.25	36.346	277.16	36.951	277.04	2- + 3-MDBF
		35.947	279.03	36.642	279.08	36.776	278.98	37.389	278.88	1-MDBF
DMDBF, peak 1	290.06	38.792	291.12	39.454	290.96	39.601	290.95	40.123	290.38	DMDBF-1
DMDBF, peak 2	292.18	39.103	292.44	39.733	292.14	39.890	292.17	40.490	291.93	DMDBF-2
C ₂ -DBF, peak 3		39.182	292.77	39.863	292.69	40.000	292.64	40.605	292.41	EDBF-1
DMDBF, peak 4	293.27	39.366	293.55	40.056	293.50	40.200	293.49	40.792	293.20	DMDBF-3
C ₂ -DBF, peak 5		39.523	294.22	40.225	294.22	40.351	294.13	40.985	294.01	DMDBF-4
DMDBF, peak 6	295.71	39.682	294.90	40.378	294.86	40.521	294.85	41.124	294.59	DMDBF-5
DMDBF, peak 7	296.35	39.858	295.64	40.540	295.55	40.627	295.30	41.284	295.27	DMDBF-6
DMDBF, peak 8	296.87	40.069	296.54	40.735	296.37	40.877	296.36	41.490	296.13	EDBF-2
C ₂ -DBF, peak 9		40.205	297.12	40.870	296.94	41.026	296.99	41.603	296.61	DMDBF-7
DMDBF, peak 10	297.44	40.291	297.48	40.981	297.41	41.115	297.36	41.740	297.19	DMDBF-8
C ₂ -DBF, peak 11		40.509	298.41	41.186	298.28	41.239	297.89	41.950	298.07	DMDBF-9
phenanthrene	300.00	40.884	300.00	41.593	300.00	41.737	300.00	42.409	300.00	phenanthrene
BN21F	353.63	52.040	353.74	52.675	353.63	52.849	353.75	53.424	353.46	BN21F
BN12F	356.16	52.567	356.28	53.197	356.16	53.280	355.84	53.945	355.98	BN12F
BN23F	358.93	53.029	358.50	53.769	358.93	53.829	358.49	54.414	358.26	BN23F
chrysene	400.00	61.644	400.00	62.256	400.00	62.410	400.00	63.015	400.00	

^aAbbreviations: DBF, dibenzofuran; DMDBF, dimethyldibenzofuran; MDBF, methyldibenzofuran; EDBF, ethyldibenzofuran; BN21F, benzo[*b*]naphtho[2,1-*d*]furan; BN12F, benzo[*b*]naphtho[1,2-*d*]furan; BN23F, benzo[*b*]naphtho[2,3-*d*]furan; I , standard retention index (eq 1); t_R , retention time (min). Peak numbers refer to Figure 3. ^bReference retention indices. The values for naphthalene, phenanthrene, and chrysene are defined values. The values for BN21F and BN12F are based on the coinjection of internal standards in this study. The other values were taken from ref 15.

EXPERIMENTAL SECTION

Rock samples were ground in a crusher to <80 mesh. About 100 g of each powdered sample was extracted for 24 h using a Soxhlet apparatus with 400 mL of dichloromethane/methanol (93:7 v/v) to obtain soluble bitumen. The extracts and oils were deasphalted 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/*n*-hexane (2:1 v/v), respectively, as eluents.

In order to obtain accurate concentrations of DBFs in crude oils and rock extracts by comparison with internal standards, the response factors of the target compounds in comparison with the labeled standards must be determined. Two labeled standards, dibenzofuran-*d*₈ (DBF-*d*₈; molecular formula C₁₂D₈O, molecular mass = 176.23; purity = 98%) and dibenzothiophene-*d*₈ (DBT-*d*₈; molecular formula C₁₂D₈S; molecular mass = 192.13; purity = 98%), and one unlabeled standard, dibenzofuran (molecular formula C₁₂H₈O; molecular mass = 168.19; purity = 98%) were used in this study. All of the labeled standards were purchased from Cambridge Isotope Laboratories (Andover, MA, USA). Dibenzofuran was purchased from Sigma-Aldrich (St. Louis, MO, USA). A series of standard mixture solutions of DBF and the labeled standards were prepared for GC–MS analyses.

The GC–MS analyses of the aromatic hydrocarbon fractions and mixture solutions were performed on an Agilent 5975i GC–MS system equipped with an HP-5 MS (5% phenylmethylpolysiloxane) fused-silica capillary column (60 m × 0.25 mm i.d. with a 0.25 μm film thickness). The GC operating conditions were as follows: (1) the temperature was held initially at 80 °C for 1 min, ramped to 310 °C at 3 °C/min, and then kept isothermal for 16 min; (2) helium was used as the carrier gas; and (3) the injector temperature was set to 300 °C. The mass spectrometer was operated in electron impact (EI) mode with an ionization energy of 70 eV and a scan range of 50–600 Da.

RESULTS AND DISCUSSION

Identification of Dibenzofuran and Methyldibenzofuran Isomers. In order to compare the retention behaviors of a given compound on different columns, the retention index system has been used.^{26,27} A commonly used retention index (I) system for temperature-programmed GC conditions for polycyclic aromatic compounds is based on a series of aromatic hydrocarbon retention markers (benzene, naphthalene, phenanthrene, chrysene, and picene, for which I = 100.00, 200.00, 300.00, 400.00, and 500.00, respectively).^{28,29} In this study, the retention indices for the m/z 168, 182, 196, and 218 isomeric compounds were calculated using following equation:²⁸

$$I = 100 \times \frac{t_{R,x} - t_{R,z}}{t_{R,z+1} - t_{R,z}} + 100z \quad (1)$$

where t_R is the retention time, x denotes the target compound, and z and $z + 1$ are the numbers of aromatic rings in the retention marker compounds eluting immediately before and after the target compound, respectively.

Figure 2 shows the distribution of isomeric m/z 168 and 182 compounds in a Lower Cretaceous oil from the Denver–Julesburg Basin, North America (sample 04049001). The DBF in the m/z 168 mass chromatogram (Figure 2a) can be identified by coinjection of an internal standard in the GC–MS analysis of the aromatic fraction (Figure 2b). The calculated retention index for DBF is 257.84, which is similar to that reported in the literature¹⁴ (Table 1). Two other compounds also elute before DBF in the m/z 168 mass chromatogram.

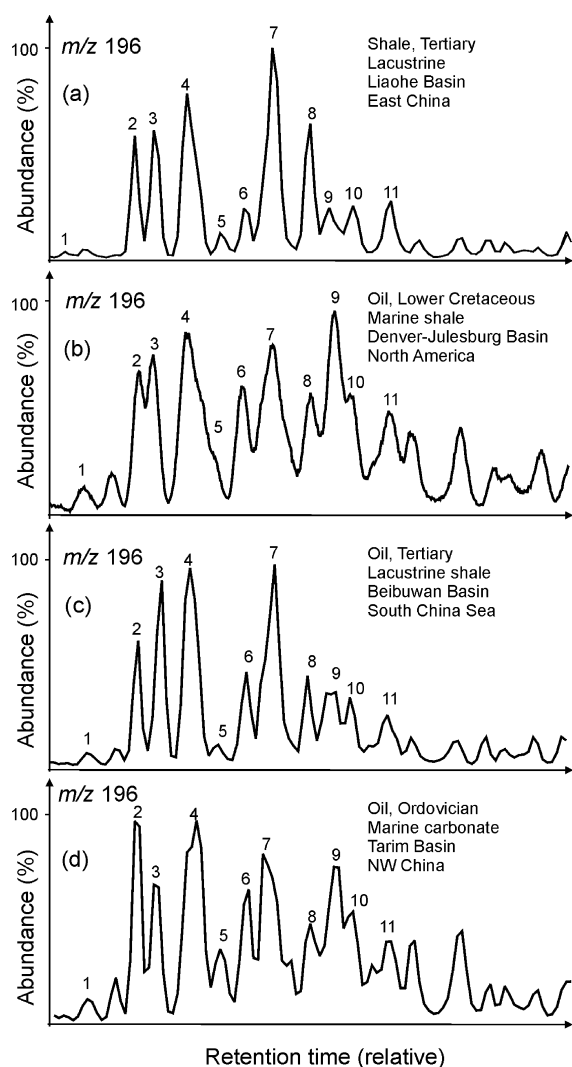


Figure 3. Mass chromatograms showing the identification and distribution patterns of dimethyldibenzofuran (m/z 196) in sedimentary rock extracts and crude oils: (a) lacustrine shale, Liaohe Basin, East China; (b) crude oil, Denver–Julesburg Basin, North America; (c) crude oil, Beibuwan Basin, South China Sea; (d) crude oil, Tarim Basin, NW China. The specific positions of the two methyl groups on DBF for each DMDBF isomer have not yet been determined. Peak numbers are assigned in Table 1.

They can be identified as 3-methylbiphenyl (3-MBP) and 4-methylbiphenyl (4-MBP) (Figure 2a) by comparison of the relative retention times to those previously reported.^{30–32}

Figure 2c shows the isomeric m/z 182 compounds in the aromatic fraction of sample 04049001. The 4-methyldibenzofuran (4-MDBF), 3,3'-dimethylbiphenyl (3,3'-DMBP), and 4,4'-dimethylbiphenyl (4,4'-DMBP) isomers can be firmly identified by comparison of their retention times to those of the coinjected internal standards (4-MDBF obtained from Chiron, Trondheim, Norway; 3,3'- and 4,4'-DMBP obtained from Sigma-Aldrich) (Figure 2d,e). Other MDBF and DMBP isomers can also be assigned by comparison of the standard retention indices and the relative retention times to those previously reported.^{7,15,30–32}

Identification of Dimethyldibenzofuran Isomers. The systematic identification and quantitation of dimethyldibenzofurans (DMDBFs) in oils and rock extracts have not been studied in previous reports because of the absence of authentic internal standards. Radke et al.¹⁵ reported the retention indices for

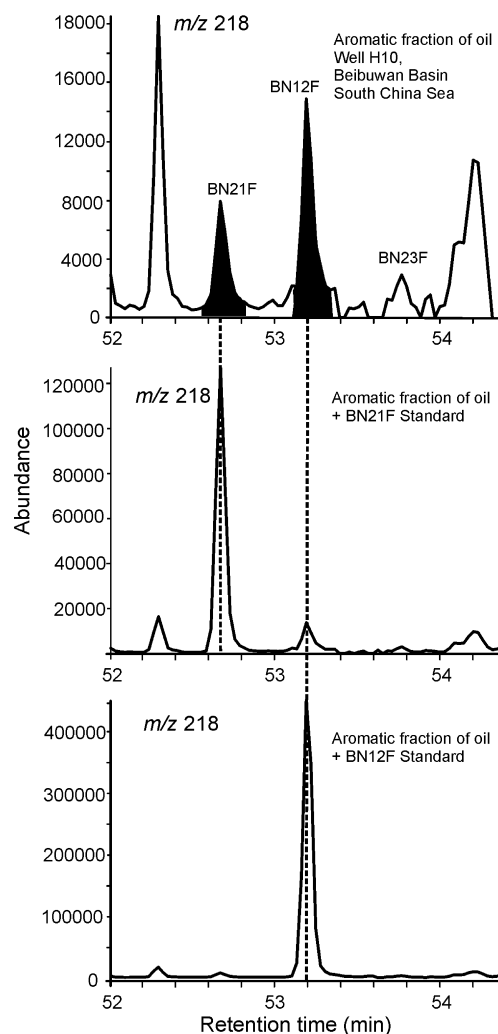


Figure 4. Mass chromatograms showing the identification of benzo[*b*]naphthofurans in an oil sample. BN21F, benzo[*b*]naphtho[2,1-*d*]furan; BN12F, benzo[*b*]naphtho[1,2-*d*]furan; BN23F, benzo[*b*]naphtho[2,3-*d*]furan. The BN23F isomer is tentatively assigned.

seven DMDBF isomers, and Armstrong¹⁶ tentatively identified 11 C_2 -dibenzofuran isomers, among which two isomers (peaks 3 and 9 in Figure 3) were inferred to be ethyldibenzofurans (Table 1). Their mass spectra show a base peak at m/z 181 ($[M - CH_3]^+$). However, the specific positions of these two methyl groups for each DMDBF isomer and the ethyl group for each EMDBF isomer were not confirmed because of the lack of commercial dimethyldibenzofuran isomers. By comparison of the retention indices and relative retention times to those reported in the literature,^{15,16} nine DMDBF and two EMDBF isomers were tentatively assigned in this study (Figure 3 and Table 1). A complete DMDBF isomer series was detected in all of the samples in our study, including rock extracts from a lacustrine shale and oils sourced from marine shale, lacustrine shale, and marine carbonate (Figure 3a–d, respectively). It seems that dimethyldibenzofurans may occur ubiquitously in crude oils and source rock extracts.

The evolution of lichens can be traced back to the Early Devonian.³³ The observation of DBFs in Ordovician carbonate-sourced oil in this study implies that lichen is not the precursor, or at least not the sole precursor, of DBFs in crude oils and ancient organic matter.

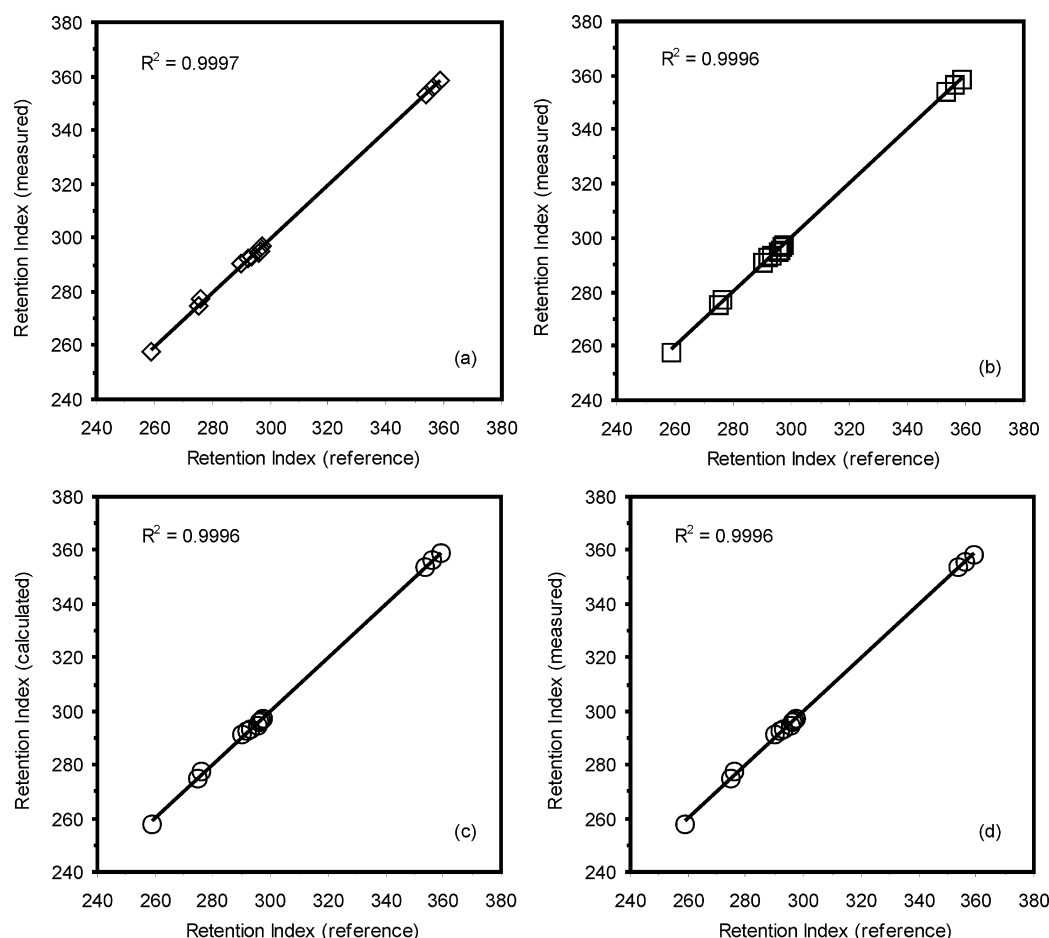


Figure 5. Plots of the measured retention indices for DBF, MDBFs, DMDBFs, and BNFs from this study versus the reference values reported in the literature¹⁵ and obtained by coinjection of internal standards in this study: (a) lacustrine shale, Tertiary, Liaohe Basin, East China; (b) crude oil, Lower Cretaceous, Denver–Julesburg Basin, North America; (c) crude oil, Tertiary, Beibuwan Basin, South China Sea; and (d) crude oil, Ordovician, Tarim Basin, NW China.

Identification of Benzo[*b*]naphthofuran Isomers. Less work has been done on the identification and application of benzo[*b*]naphthofurans (BNFs) in petroleum geochemistry. The GC retention behavior of benzo[*b*]naphthofuran isomers has not been reported to date. In this study, two isomers, benzo[*b*]naphtho[2,1-*d*]furan (BN21F) and benzo[*b*]naphtho[1,2-*d*]furan (BN12F), were detected in oils by coinjection of appropriate internal standards (Community Bureau of References, Geel, Belgium) in the GC–MS analyses of the aromatic fractions of oils (Figure 4). Another isomer, benzo[*b*]naphtho[2,3-*d*]furan (BN23F) can also be identified, even though no authentic internal standard was coinjected in this study. Benzo[*b*]naphthofuran and benzo[*b*]naphthothiophene (BNT) have similar molecular structures, differing only by one atom in the bridge of the furan ring: oxygen in BNF versus sulfur in BNT (Figure 1). Oxygen and sulfur atoms are both highly electronegative. The elution order of methyl dibenzofuran isomers in the mass chromatogram is exactly the same as that of methyl dibenzothiophene isomers (i.e., 4-, 2-, 3-, and 1-substituted homologues), and the 2- and 3-substituted isomers typically coelute in the mass chromatograms.⁷ The elution sequence of benzo[*b*]naphthothiophene isomers in the *m/z* 234 mass chromatogram is benzo[*b*]naphtho[2,1-*d*]thiophene ([2,1]BNT), benzo[*b*]naphtho[1,2-*d*]thiophene ([1,2]BNT), and benzo[*b*]naphtho[2,3-*d*]thiophene ([2,3]BNT).²⁴ Thus, BN23F can be reasonably identified (Figure 4) by comparison with the distribution

pattern and relative retention times of the benzo[*b*]naphthothiophene isomers. The elution sequence and relative retention times for BNF isomers in our study are comparable to those reported by Armstrong.¹⁶

The structures of BN21F and BN12F (Figure 1) are similar to those of benzo[*a*]carbazole (B[*a*]CA) and benzo[*c*]carbazole (B[*c*]CA), respectively, which occur in oils in significant quantities. The B[*a*]CA/(B[*a*]CA + B[*c*]CA) ratio in oils has been used as an empirical measure of relative secondary migration distance.³⁴ The main mechanism is that the B[*a*]CA molecule, which is more elongated compared with the subspherical B[*c*]CA molecule, is preferentially removed from oils onto clay mineral surfaces and into solid organic matter in the carrier bed. The results of that previous study³⁴ suggest that functionalized aromatic compounds with polarity/shape differences between isomers may be suitable molecular indicators for monitoring oil migration, and the [2,1]BNT/([2,1]BNT + [1,2]BNT) ratio has been proven to be an effective geochemical indicator for tracing oil migration pathways.³⁵ Therefore, because of the structural similarity of BN21F and BN12F to B[*a*]CA and B[*c*]CA, respectively, the BN21F/(BN21F + BN12F) ratio may also be a potential molecular geochemical parameter to indicate oil migration routes and distances.

The measured retention data for DBF, MDBFs, DMDBFs, and BNFs in all of the samples in this study show excellent correlations with those obtained by coinjection of internal

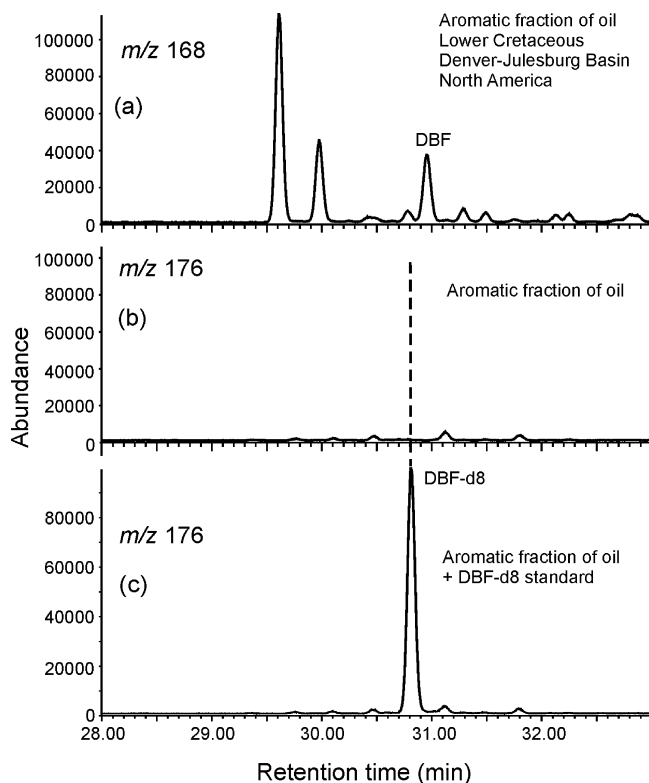


Figure 6. (a) m/z 168 mass chromatogram. (b, c) Correlation of the m/z 176 mass chromatograms of the aromatic fraction of an oil sample (b) without and (c) with coinjection of the internal standard DBF- d_8 .

standards and reported in the literature,¹⁵ with coefficients higher than 0.999 (Figure 5). The differences between the measured values in this study and the previously reported retention index values for all compounds are within ± 1.1 index unit. On the basis of our practical experience,²⁴ retention indices within ± 1.1 index units are acceptable.

Quantitative Analysis of DBFs in Oils and Sediment Extracts. Because oils and rock extracts are complex mixtures of numerous compounds, it was necessary to ensure that the internal standards DBF- d_8 and DBT- d_8 do not interfere with other compounds in the corresponding mass chromatograms. Figure 6b,c shows the m/z 176 mass chromatograms for the oil sample 04049001 before and after coinjection of the internal standard DBF- d_8 , respectively. It is clear that no other

compound peaks coelute with the DBF- d_8 peak in the m/z 176 trace. A previous study also showed that no other compound peaks interfere with the DBT- d_8 peak in the m/z 192 mass chromatogram.²⁴

Furthermore, we can calibrate DBF- d_8 against a known amount of natural DBF. This calibration allows the determination of the response factor (RF) relating the response of natural DBF to labeled DBF- d_8 according to the following equation:

$$RF = \frac{(A_{DBF}/C_{DBF})}{(A_{DBF-d_8}/C_{DBF-d_8})} = \left(\frac{A_{DBF}}{A_{DBF-d_8}} \right) \times \left(\frac{C_{DBF-d_8}}{C_{DBF}} \right) \quad (2)$$

where A is the area of a peak in the mass chromatogram and C is the concentration of the corresponding compound. Thus, the area ratio A_{DBF}/A_{DBF-d_8} is equal to the concentration ratio C_{DBF}/C_{DBF-d_8} multiplied by the RF. A set of A_{DBF}/A_{DBF-d_8} ratio data can be obtained by GC–MS analyses of a series of standard solutions with different DBF/DBF- d_8 concentration ratios. Figure 7a shows a cross-plot of A_{DBF}/A_{DBF-d_8} versus C_{DBF}/C_{DBF-d_8} calculated from the total ion current (TIC) chromatogram. The slope of the line obtained by least-squares linear regression of the data is the RF. Here the RF relating to the response of natural DBF to the internal standard DBF- d_8 is 1.11 (Table 2). This result is reasonable because of the much

Table 2. Response Factors Relating the Response of Dibenzofurans and Benzo[*b*]naphthofurans to Labeled Internal Standards in GC–MS Analysis

method	compound	response factor	
		labeled DBF- d_8	labeled DBT- d_8
TIC	DBF	1.11	1.13
m/z 168	DBF	1.17	1.14
m/z 182	MDBF	0.68	0.71
m/z 196	DMDBF	0.94	1.00
m/z 218	BN21F	0.81	0.86
m/z 218	BN12F	0.85	0.91

smaller differences in the probabilities for removal of a hydrogen or deuterium atom in aromatic compounds.²⁵ The deviation from 1.00 is partially due to the difference between the molar masses of unlabeled DBF and labeled DBF- d_8 : there are more moles of unlabeled DBF in a given mass of compound than in the same mass of DBF- d_8 , and therefore, it is expected

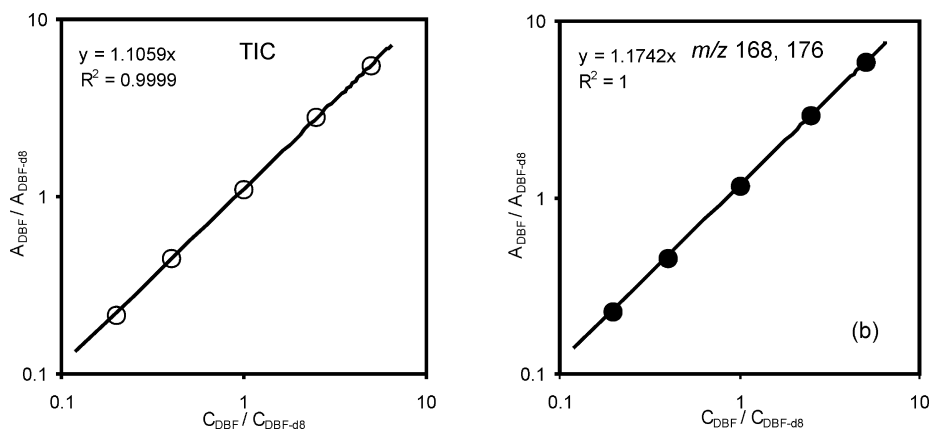


Figure 7. Cross-plots of A_{DBF}/A_{DBF-d_8} vs C_{DBF}/C_{DBF-d_8} based on (a) total ion current (TIC) and (b) mass chromatograms.

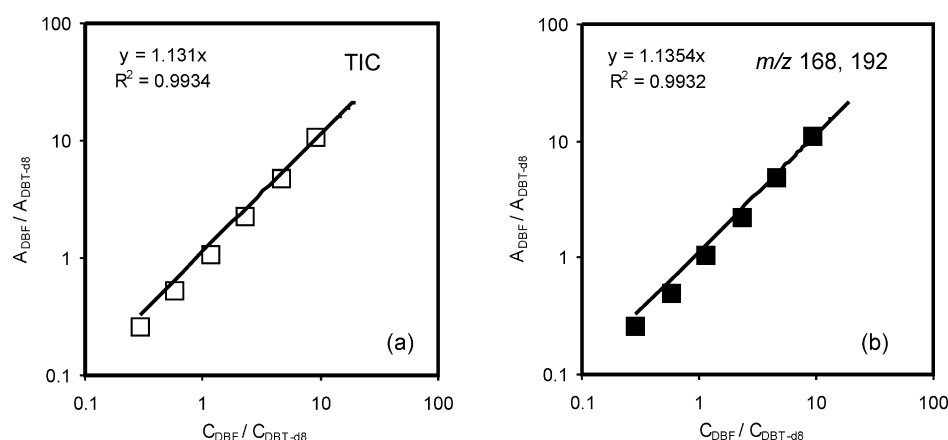


Figure 8. Cross-plots of $A_{\text{DBF}}/A_{\text{DBT-d}_8}$ vs $C_{\text{DBF}}/C_{\text{DBT-d}_8}$ based on (a) total ion current (TIC) and (b) mass chromatograms.

Table 3. List of Oil and Rock Samples Analyzed in This Study

well/sample no.	type	basin	country	age of source rocks	lithology of source rocks
04049001	oil	Denver–Julesburg	USA	Lower Cretaceous	marine shale
H10	light oil	Beibuwan	China	Tertiary	fluvial/delta shale
H12-3	light oil	Beibuwan	China	Tertiary	fluvial/delta shale
Tuo119	oil	Liaohe	China	Tertiary	lacustrine shale
S203	oil	Liaohe	China	Tertiary	lacustrine shale
TP17	oil	Tarim	China	Ordovician	marine carbonate
Dib-1	oil	Termit	Niger	Upper Cretaceous	marine shale
FW-1	oil	Termit	Niger	Upper Cretaceous	marine shale
GW-1	oil	Termit	Niger	Upper Cretaceous	marine shale
HD-1	core	Beibuwan	China	Tertiary	fluvial/delta shale
SG-1	cuttings	Liaohe	China	Tertiary	lacustrine shale
H-1	core	Termit	Niger	Upper Cretaceous	marine shale
Woodford	outcrop	Oklahoma	USA	Devonian	marine shale
LN46	core	Tarim	China	Ordovician	marine carbonate

that unlabeled DBF should give a larger signal. The molar ratio of DBF- d_8 to DBF is $176/168 = 1.05$, which is close to the RF of 1.11 measured in this study. The difference between the measured and calculated response factors may be attributed to partial coelution of DBF- d_8 and DBF peaks in TIC chromatograms, as DBF- d_8 elutes slightly before unlabeled DBF and cannot be completely separated from it. Actually, we observed a small amount of m/z 176 ion in the spectrum of DBF, which must be contributed by DBF- d_8 . Therefore, the measured response factor is a little higher than the calculated value.

It is worth noting that DBF is typically identified and quantitated by integration of mass chromatograms of the main fragment ion at m/z 168 (the base peak ion for DBF) with that at m/z 176 (the base peak ion for DBF- d_8) using standard GC–MS techniques. A correction should be made to account for the intensities of the fragment ions relative to the total ion current in the spectra of the compounds quantitated and the standard.³⁶ The difference can also be simply evaluated by comparison of the response factors calculated using fragment chromatograms and the TIC chromatogram. Figure 7b shows a cross-plot of $A_{\text{DBF}}/A_{\text{DBF-d}_8}$ versus $C_{\text{DBF}}/C_{\text{DBF-d}_8}$ determined from the m/z 168 and 176 mass chromatograms. The response factor calculated from these data is 1.17, which is slightly higher than that determined from the TIC chromatogram. The intensity of the base peak ion of DBF (m/z 168) accounts for 44.1% of the total ion current, and the base peak ion of DBF- d_8 (m/z 176) is 41.2% relative to the total ion intensity. On a molar basis, it can be expected that unlabeled DBF should give a larger signal than

an equivalent amount of labeled DBF- d_8 . The intensity ratio is $44.1/41.2 = 1.07$. Thus, the response factor relating DBF to DBF- d_8 should be $1.05 \times 1.07 = 1.12$, which is close to the value of 1.17 measured in this study. Therefore, the peak area to concentration calculation for DBF in the unknown samples must be corrected by dividing the area of the DBF peak in the fragment chromatograms by 1.17.

The internal standard dibenzothiophene- d_8 (DBT- d_8) was used herein to examine the response factor of DBF to this sulfur-heterocyclic aromatic thiophenic compound according to an expression analogous to eq 2 (with “DBF- d_8 ” replaced by “DBT- d_8 ”). Figure 8a,b shows the cross-plots of $A_{\text{DBF}}/A_{\text{DBT-d}_8}$ versus $C_{\text{DBF}}/C_{\text{DBT-d}_8}$ determined from the TIC and fragment chromatograms, respectively. Here the corresponding response factors relating the responses of the unlabeled DBF to DBT- d_8 are 1.13 and 1.14, respectively (Figure 8 and Table 2). The similarity between the regression slopes suggests that the intensities of the molecular ion peaks (M^+ , base peak ion) for DBF (m/z 168) and DBT- d_8 (m/z 192) may constitute nearly the same proportion relative to their respective total ion intensities. The deviation from 1.00 may be due to the difference in the molar masses of unlabeled DBF and DBT- d_8 . The molar mass ratio for DBT- d_8 to DBF is $192/168 = 1.14$, which is within the calculation error for the values measured in this study. In view of the fact that the response factors relating DBF to labeled DBT- d_8 obtained from the fragment and TIC chromatograms are equivalent and that the molecular structures of DBT and DBF are quite similar, labeled DBT- d_8

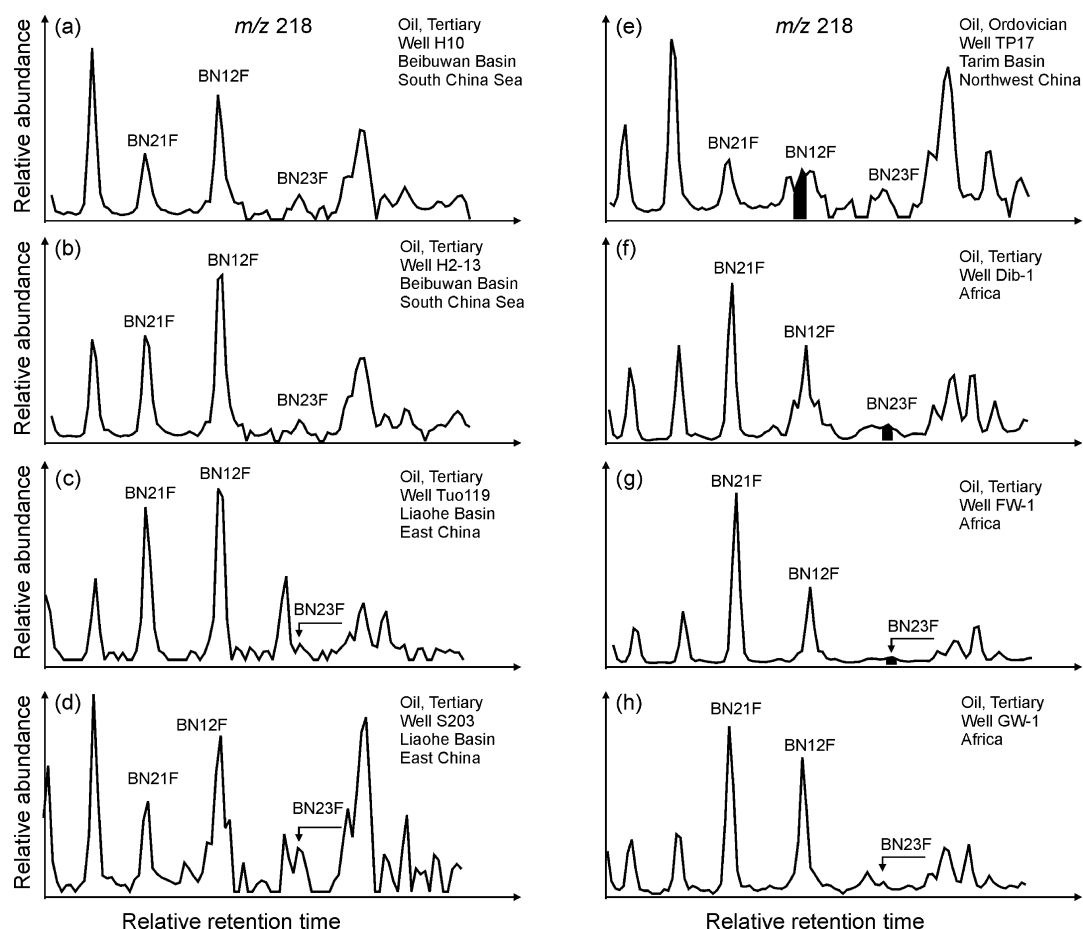


Figure 9. m/z 218 mass chromatogram distribution patterns of BNFs in oils from (a, b) fluvial/delta shale, Beibuwan Basin, South China Sea; (c, d) lacustrine shale, Tertiary, Liaohé Basin, East China; (e) marine carbonate, Tarim Basin, NW China; and (f–h) marine shale, Niger, Africa.

is an optimal internal standard for quantitative analyses for both dibenzothiophene and dibenzofuran in oils and rock extracts.

Using the same approach, we can calculate the response factors relating the responses of 4-MDBF to DBF- d_8 and DBT- d_8 by fragment chromatograms. They are 0.68 and 0.71, respectively (Table 2). Because the mass spectrometric response is the same for all methyl-dibenzofuran isomers, we can use these factors to quantify other methyl-dibenzofuran isomers in oils and rock extracts. The response factors relating the responses of all dimethyl-dibenzofuran isomers to DBF- d_8 and DBT- d_8 are estimated to be 0.94 and 1.00, respectively (Table 2). The response factors relating the responses of BN21F to DBF- d_8 and DBT- d_8 by fragment chromatograms are 0.81 and 0.86, respectively, and those of BN12F to DBF- d_8 and DBT- d_8 are 0.85 and 0.91, respectively (Table 2).

The absolute concentrations ($\mu\text{g/g}$ of oil) of DBF, MDBFs, and DMDBFs can be obtained by comparison of their peak areas with that of the internal standard (DBF- d_8 or DBT- d_8) and then dividing by the corresponding response factor. The concentrations of total DBFs (including the parent and all of the methyl-, dimethyl-, and ethyldibenzofuran isomers) in oils derived from the siliciclastic lacustrine source rocks in the Beibuwan Basin, South China Sea, range from 268 to 883 $\mu\text{g/g}$ of oil, with an average of 518 $\mu\text{g/g}$, which is about 5 times the concentration found in the oils from carbonate source rocks in the Tarim Basin, Northwest China (104 $\mu\text{g/g}$). Accurate quantitative analysis of DBFs

and BNFs is vital for their application in studies of depositional environment, thermal maturity of ancient organic matter, and oil migration.

Distribution of BNFs in Oils and Sediment Extracts. In this study, we analyzed some oils sourced from typical marine carbonate, marine and lacustrine shales, and fluvial/deltaic shales (Table 3). All of the oil samples investigated in this study have measurable amounts of BN21F and BN12F isomers (Figure 9), which indicates the ubiquitous occurrence of BNF in crude oils. The oils of marine carbonate origin have a relatively lower abundance of BNF compounds (Figure 9e) compared with those from clastic source rocks (Figures 9a–d,f–h), which is consistent with the distribution of DBFs. In all of the oils, the BN23F isomer is present in very low concentrations or is below the detection limit.

Furthermore, some rocks deposited in various environments were also analyzed. Figure 10 illustrates the distribution patterns of sedimentary rock extracts. BNF isomers occur in all of the rock extracts. Unlike oils, the BN23F isomer is present in significant concentrations in rock extracts from marine shales (Figure 10a,d). The marine carbonate rocks also have relatively low abundance of BNF isomers, which is consistent with the related oils (Figure 9e).

The precursors and origin of BNFs in crude oils and sedimentary rock extracts have not been previously reported. It appears that BNFs in oils and sediment extracts may not have distinct biological precursors. They may be derived from reactions of other compounds in organic matter.

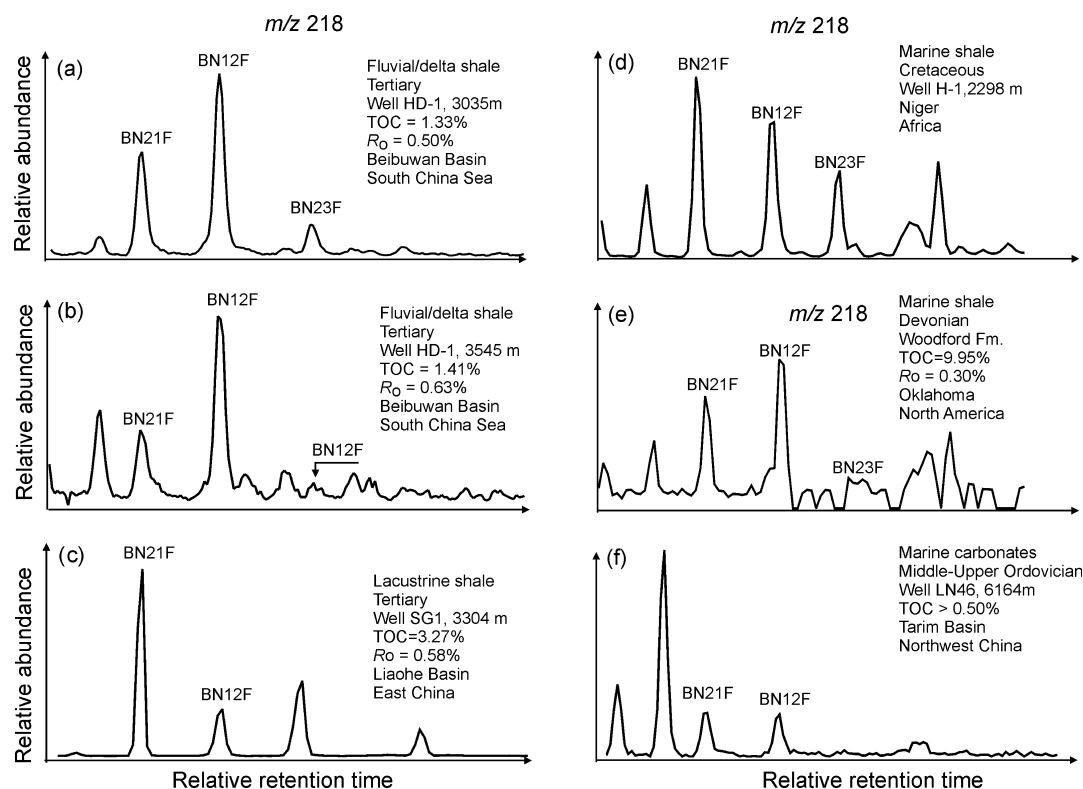


Figure 10. m/z 218 mass chromatogram distribution patterns of BNFs in sedimentary rock extracts from (a) and (b) fluvial/delta shale, Beibuwan Basin, South China Sea; (c) lacustrine shale, Tertiary, Liaohe Basin, East China; (d) marine shale, Cretaceous, Niger, Africa; (e) Woodford marine shale, Devonian, North America; and (f) marine carbonate, Tarim Basin, NW China.

CONCLUSIONS

Dibenzofuran (DBF), its methyl-, dimethyl-, ethyl-substituted derivatives, and isomers of benzo[*b*]naphthofuran (BNF) have been systematically identified in crude oils and rock extracts by comparison with mass spectrometric data for reference standards and published retention indices. Quantitative analysis of dibenzofuran was performed by coinjection of deuterium-labeled standards. The response factors relating the responses of the natural DBF to per-deuterated dibenzofuran (DBF- d_8) and dibenzothiophene (DBT- d_8) were obtained using a series of mixture solutions with different concentration ratios. These response factors can be applied for area calibration of DBF and BNF compounds in GC–MS analyses.

The concentration of the total DBFs in oils derived from the siliciclastic lacustrine source rocks in the Beibuwan Basin, South China Sea, averages 518 $\mu\text{g/g}$, which is about 5 times that in the oils from carbonate source rocks in the Tarim Basin, Northwest China. BNFs ubiquitously occur in oils and source rocks of various depositional environments. The distribution patterns of BNFs in sedimentary rock extracts and oils have been investigated. The BN21F/(BN21F + BN12F) ratio is herein proposed as a potential molecular geochemical parameter to indicate oil migration routes and distances.

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Notes

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