

The application of carbon isotope compositions of fluorene and its methylated homologues in the sources and depositional environments of sedimentary organic matter

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Abstract Analysis of the carbon isotope composition ($\delta^{13}\text{C}$) of individual polycyclic aromatic compounds (PACs) in sedimentary organic matter (OM) and oils is increasingly important in organic geochemistry, as it provides information on OM sources, thermal maturity, and secondary alteration. In this study, the $\delta^{13}\text{C}$ values of fluorene (Flu) and its methylated homologues were investigated in coal extracts and crude oils from various depositional environments (lacustrine shale, marine shale, marine carbonate, and terrestrial coal). The results show that the $\delta^{13}\text{C}$ values of Flu and 1-methylfluorene (1-MF) are primarily affected by the origin of OM and are less related to thermal maturity, which indicates a variety of depositional environments. Two cross-plots of the $\delta^{13}\text{C}$ values for Flu and 1-MF versus the pristane/phytane ratio (Pr/Ph) are used to investigate the effects of the depositional environments and sources of OM. These cross-plots classify the study samples into five environmental/source zones: marine, algae; lacustrine, algae-bacterial mixed; deltaic/lacustrine/coastal, mixed and aquatic-dominated; transitional (marine and terrestrial), mixed and terrigenous-dominated; and coal, terrigenous. The samples from the various depositional environments and sources are distinguishable, particularly those of marine and transitional facies with similar paleoenvironments. The results provide

useful tools to discriminate between OM derived from different sources with different levels of marine and terrestrial input.

Keywords $\delta^{13}\text{C}$ values · Individual aromatic compounds · Fluorene · 1-Methylfluorene · Depositional environment · Source

1 Introduction

The geochemical significance of the stable carbon isotope ($\delta^{13}\text{C}$) in sedimentary organic matter (OM) and crude oil has been widely studied (Sofer 1984; Radke et al. 1998; Galimov 2006; Maslen et al. 2011; Cesar and Grice 2017; Karp et al. 2020). In recent years, compound-specific isotope analysis has come to play a key role because it provides useful information about the source(s) of individual compounds in complex mixtures (Grice et al. 2001; Maslen et al. 2011; Karp et al. 2020).

Analysis of the $\delta^{13}\text{C}$ of individual compounds using compound-specific isotope analysis (CSIA) is widely employed to identify the sources of saturated compounds such as *n*-alkanes and cadinanes (Boreham et al. 1994; Murray et al. 1998), and oil–source correlations are often carried out based on the $\delta^{13}\text{C}$ values of sedimentary OM (Cai et al. 2015). However, precisely determining the carbon isotopic composition of individual aromatic compounds is challenging due to interference between the compounds in complex mixtures. Recent studies have established a process for the separation of different aromatic components and the determination of isotopes of individual compounds (Jiang et al. 2013; Konan et al. 2022; Niu et al. 2023) and have developed several indices for identifying the sources of OM based on test results. Several studies have also confirmed

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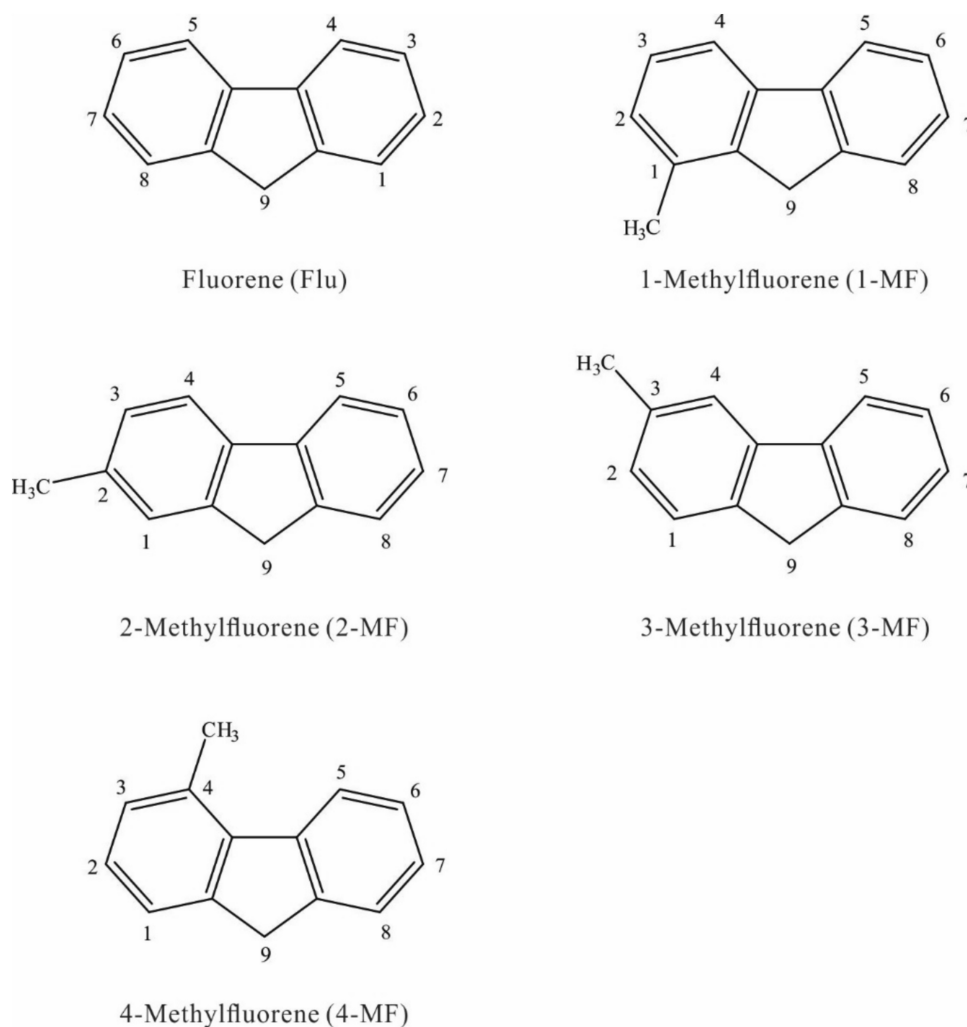
that the values of individual aromatic compounds—including 1,6-dimethylnaphthalene (DMN), 1,2,5-trimethylnaphthalene (TMN), 1,3,6,7-tetrimethylnaphthalene (TeMN), 1-methylphenanthrene (MP), 1,9-dimethylphenanthrene (DMP), and some biomarkers such as retene and dehydroabietic acid methyl ester (DAME)—are crucial for determining the origins of OM (Maslen et al. 2011; Le Métayer et al. 2014; Cesar and Grice 2017) and reconstruction of the paleoenvironment (Grice et al. 2001; Karp et al. 2020; Zakrzewski et al. 2024).

Fluorene (Flu) and its alkylated homologues are important polycyclic aromatic compounds (PACs) (Fig. 1) in oil, coal, and sedimentary rocks (Asif et al. 2009, 2010; Li et al. 2013a, 2018), and their distribution patterns and relative concentrations are widely applied in depositional environments for analyzing sedimentation of OM and identification of oil migration pathways (Hughes et al. 1995; Li et al. 2013a; Fang et al. 2016; Yang et al. 2017). Because of their similar chemical structures, several studies have been conducted to investigate the geochemical applications of Flu,

dibenzothiophene (DBT), and dibenzofuran (DBF) series, such as the use of ternary diagrams based on their relative abundance (Li et al. 2013b; Asif and Wenger 2019). Indicators established by their methylated homologues (Hughes et al. 1995; Yang et al. 2017) are also widely applied as molecular indicators to distinguish various depositional environments and carry out oil-to-oil and oil-to-source correlation. However, there has been little work on the origins of Flu, DBT, and DBF and their methylated homologues in oil and sedimentary OM. Specific origins for Flu and DBT have not yet been proposed. Previous studies have shown that DBF and methyldibenzofurans (MDBFs) are mainly derived from lichens, fungi, and higher plants (Radke et al. 2000; Millot et al. 2016; Liang et al. 2024). It has been proposed that a hypothesis for the sedimentary reactions in the formation of heterocyclic aromatic hydrocarbons can be developed based on laboratory experiments (Asif et al. 2010; Li et al. 2013b).

In this study, a chromatography column was used to separate Flu and its methylated homologues, the isolated target

Fig. 1 Structures of fluorene and methylfluorenes



compounds of which were subsequently subjected to CSIA. The significance of the $\delta^{13}\text{C}$ of Flu and 1-methylfluorene (1-MF) in the compounds was studied using their individual stable carbon isotopic compositions. The results will improve our understanding of their potential to distinguish the depositional environments and sources of OM.

2 Samples and geological setting

Ten crude oils were collected from the Baiyun Depression in the Zhujiangkou Basin (South China) and five coals from the Ordos Basin (north-central China). The other samples used in this study were 15 Paleogene deep freshwater lacustrine oils from the Fushan Depression in the Beibuwan Basin (South China Sea), 11 Ordovician marine carbonate oils from the Shunbei oilfield in the Tarim Basin (Northwest China), 12 marine shale crude oils from the Termit Basin (Eastern Niger), and eight anoxic lacustrine crude oils from the Bongor Basin.

The Ordos Basin is an intracratonic depression basin located in north-central China, with $250 \times 103 \text{ km}^2$ of Paleozoic strata (Dai et al. 2005; Yang et al. 2005). Its Carboniferous–Permian strata are composed of coal seams, black shales, and sandstones and are mainly deposited in marine–terrestrial transitional facies. The Upper Paleozoic strata in the southeast of the basin were affected by hydrothermal activity during the Early Cretaceous (Yang et al. 2005; Li and Gao 2010). A suite of five coal samples was collected from Carboniferous–Permian coal measure strata in the basin (Fig. 2a).

The Baiyun Sag is located in the northern continental margin of the South China Sea. It is the largest sedimentary sag in the Pearl River Mouth Basin, with an area of more than $14,000 \text{ km}^2$ (Fu et al. 2020), deposited in a deepwater slope region and surrounded by the Panyu Low Uplift, the Dongsha Uplift, the Yunli Low Uplift, and the Yunkai Low Uplift (Sun et al. 2020). Ten light oils were collected from three regions: four samples from the Panyu Low Uplift (PLU), three from the northeastern Baiyun Sag region (NEBS), and three from the eastern Baiyun Sag region (EBS). The samples originated from source rocks deposited in lacustrine and deltaic-coastal environments (Fig. 2b).

The 2920 km^2 Fushan Depression is in the northern continental shelf of the South China Sea and is one of a number of secondary tectonic units situated in the southeastern margin of the Beibuwan Basin. The Paleogene sequence in the depression is divided into three formations: the Changliu Formation, the Liushagang Formation, and the Weizhou Formation. The Changliu and Weizhou formations are mainly deposited in fluvial-alluvial facies. The Liushagang Formation (Els) contains the most important source rocks and reservoirs, mainly developed in delta

lacustrine facies with an oxidizing environment (Zeng et al. 2021). Fifteen crude oils were collected from pools in the Liushagang Formation originating from source rocks deposited in typical lacustrine environments (Fig. 2c).

The Shuntogol area is located in the central part of the Tarim Basin. It is divided into the Shaya and Katak uplifts from north to south and the Mangar and Awati depressions from east to west. The Ordovician strata are well developed and comprise the Penglaiba Formation (O_{1p}), the Yingshan Formation (O_{1y}), the Yijianfang Formation (O_{2yj}), the Chalbak Formation (O_{3q}), the Lianglitage Formation (O_{3l}) and the Sangtamu Formation (O_{3s}), from bottom to top. The hydrocarbon exploration and development strata in the area are mainly carbonate rocks of the Yijianfang Formation and the upper Yingshan Formation. Eleven light oil samples were collected from Shunbei reservoirs, which are considered to have been generated from O_{1y} and O_{2yj} marine carbonates (Fig. 2d).

The Termit Basin is an extensional asymmetric rift basin in the West and Central African Rift System with an area of approximately $27,000 \text{ km}^2$. The main depression has a length of nearly 300 km and a width of ~60–110 km (Liu et al. 2012). The basement is Precambrian–Jurassic metamorphic rock, overlaid by Cretaceous–Quaternary strata. The Upper Cretaceous strata are composed of shallow marine shale, silts, and sand, which were mainly deposited during a period of large-scale marine transgression. Twelve crude oils were collected from the Termit Basin, which are considered to derive from the transitional area of an epicontinental sea affected by transgression (Fig. 2e).

The Bongor Basin is a significant petroliferous basin in Chad with an area of $1.8 \times 104 \text{ km}^2$. It is a Mesozoic–Cenozoic continental rift basin located in the Central African Shear Zone (CASZ), which developed from the Central Africa dextral strike-slip fault. It is divided from south to north into four secondary structural units: the southern depression, the southern uplift, the central depression, and the northern slope. Major oil accumulations have been discovered in the northern slope, including the Baobab, Mimosa, Ronier, and Prosopis oilfields (Wang et al. 2023). A total of eight oil samples were collected from the Lower Cretaceous in the major oilfields of the northern slope, which originated from source rocks deposited in typical lacustrine environments and are characterized by biodegradation (Fig. 2f).

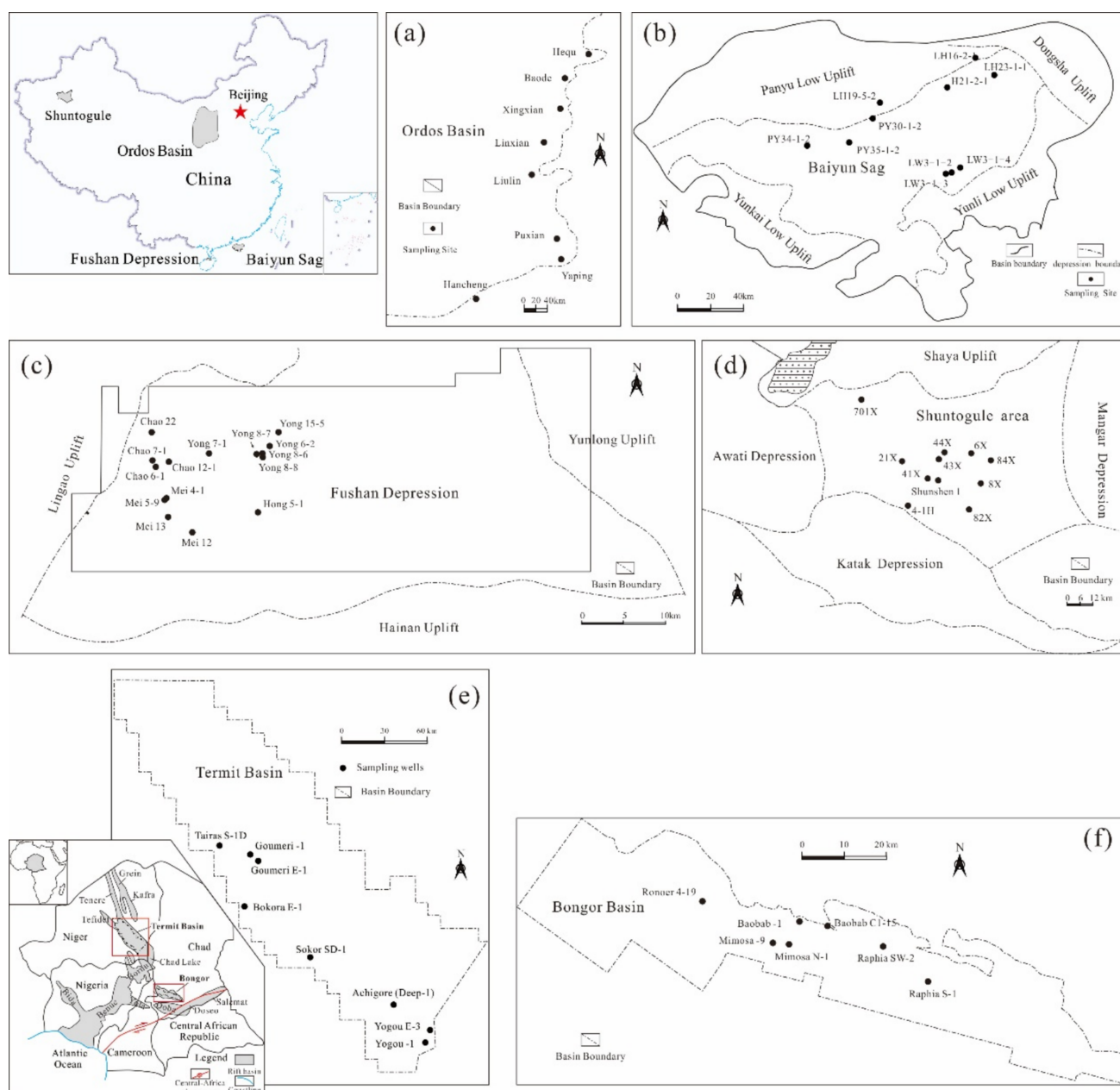


Fig. 2 Sampling sites of coals and oils

3 Methods and materials

3.1 Coal extraction and gas chromatography–mass spectrometry (GC–MS) analysis

The analytical procedures used follow those set out in Zhu et al. (2019). The coal samples were crushed, ground to <80 mesh (0.2 mm), and processed for 48 h using a Soxhlet apparatus with 400 mL of dichloromethane to extract soluble OM. The coal extracts were filtered using petroleum ether to remove asphaltenes. The solutions were then separated into

saturated, aromatic, and resin fractions using a silica gel/alumina chromatography column with petroleum ether, dichloromethane/petroleum ether (2:1, v/v), and dichloromethane/methanol (93:7, v/v), respectively, as the elution solvents.

GC–MS analyses of the aromatic fractions of the coal extracts and oils and comparisons with authentic standards were conducted using an Agilent 6890 gas chromatograph coupled to an Agilent 5975i mass spectrometer equipped with an HP-5MS fused silica capillary column (60 m × 0.25 mm i.d., 0.25 μm film thickness). GC–MS analyses of the saturated fractions were conducted under

the following conditions: the initial GC oven temperature was maintained at 50 °C for 1 min, then increased to 120 °C at a rate of 20 °C/min, then increased from 120 to 310 °C at 3 °C/min, and finally held constant for 25 min. For the aromatic fractions and the authentic standards, the initial temperature of the GC oven was set at 80 °C, which was maintained for 1 min, then gradually increased to 310 °C at 3 °C/min, and finally held constant for 16 min. Helium was used as the carrier gas, and the temperature of the split injector was set at 300 °C. The MS was operated with the electron ionization (EI) source set at 70 eV and the scan range at m/z 50–600.

3.2 Sub-separation of aromatic compounds

Sixty-one coal and oil samples were selected for sub-separation and isotopic analysis. The aromatic compounds obtained from the previous separation were further separated into one-ring, two-ring, three-ring, and four-ring and larger aromatic compounds. The first step was to prepare the column. A small amount of pre-extracted cotton wool was placed at the bottom of a glass column, preventing leakage of the stationary phase. The glass column was used as the separation column (20 cm in length and 10 mm inner diameter). Extracted alumina (obtained from Sigma-Aldrich) and pre-extracted silica were both activated at 110 °C for 4 h. Then, 2–3 g of the active alumina and an equal volume of silica were inserted into the glass column, which was carefully knocked to ensure even distribution of the alumina. The aromatic compounds were then transferred into the top of the column. The column was eluted using petroleum ether/dichloromethane (93:7, V:V, 6 mL), petroleum ether/dichloromethane (9:1, V:V, 8 mL), petroleum ether/dichloromethane (3:1, V:V, 8 mL), and dichloromethane (8 mL), sequentially, for the one-ring, two-ring, three-ring, and four-ring and larger aromatic fractions. The two- and three-ring fractions of the representative sample are shown in Fig. 3. The Flu and MFs were purified to detect the individual stable carbon isotope.

3.3 Gas chromatography–isotope-ratio mass spectrometry (GC-IRMS)

A total of 0.5 μL of the aromatic sub-fraction was injected into the inlet of an Agilent 7890 GC-GC5 interface precision IRMS (Elementar analyzer system) operated in split mode. Separation was carried out on an AB-PONA column, 50 m long, 0.20 mm in diameter, and with a film thickness of 0.50 μm . The temperature program for detection of the two-ring fractions was 100 °C for 1 min, increasing to 180 °C at a heating rate of 15 °C/min, then increasing to 270 °C at 1.5 °C/min, ramping again to 310 °C at a rate of 15 °C/min, then holding at 310 °C for 15 min. The procedure for

detecting the three-ring fractions was holding at 100 °C for 1 min, increasing to 200 °C at 15 °C/min, increasing at 2 °C/min to 290 °C, ramping to 310 °C at 10 °C/min, and finally holding at 310 °C for 20 min. The temperature of the oxidation oven was 850 °C, and helium was used as the carrier gas.

The accuracy of the data before and after sample analysis was routinely monitored against a set of standards of known isotopic composition. The stable carbon isotope data were evaluated against *n*-alkanes with known $\delta^{13}\text{C}$ values obtained from the Biogeochemical Laboratories of Indiana University. One injection of standards was performed for every five sample injections. A CO_2 reference gas standard was calibrated to the *n*-alkane mixture standard (calibrated to Vienna Pee Dee Belemnite, VPDB) and analyzed in IRMS. The resulting data are presented in delta notation relative to the international standard (VPDB). Every sample was injected at least twice, and the carbon isotope data of the selected polycyclic aromatic components were analyzed at an average standard deviation of 0.5‰.

4 Results and discussion

4.1 Identification and distribution of Flu and MFs

The distribution of Flu and MF isomers in oil and coal extracts is shown in Figs. 4 and 5. Flu and four MF isomers, namely 2-, 3-, 1-, and 4-MF, typically elute in the m/z 166 and m/z 180 mass chromatograms of aromatic fractions of coal extracts and oils. Flu and the four MF isomers can be identified by comparing the relative retention times and retention indices shown on the m/z 166 and m/z 180 mass chromatograms with those published in previous research (Radke et al. 1982; Pu et al. 1990).

In this study, crude oil samples from various depositional environments were examined. Flu and the four MF isomers occur in all the oil and coal samples (Figs. 4 and 5). All samples show relatively high abundance of Flu and 1-MF on the m/z 166 and m/z 180 mass chromatograms. The abundance of 2-, 3-, and 4-MF is lower than that of 1-MF in all the oil and coal samples.

4.2 Factors controlling $\delta^{13}\text{C}$ of Flu and 1-MF

Flu occurs widely in oils and coal extracts, forming important polycyclic aromatic compounds as well as MF homologues. Previous studies have determined that the distribution and relative abundance of Flu and MFs in petroleum and sediments is closely related to freshwater lacustrine facies, which may be related to the abundant methylene species in this type of environment (Li et al. 2013b; Asif and Wenger 2019).

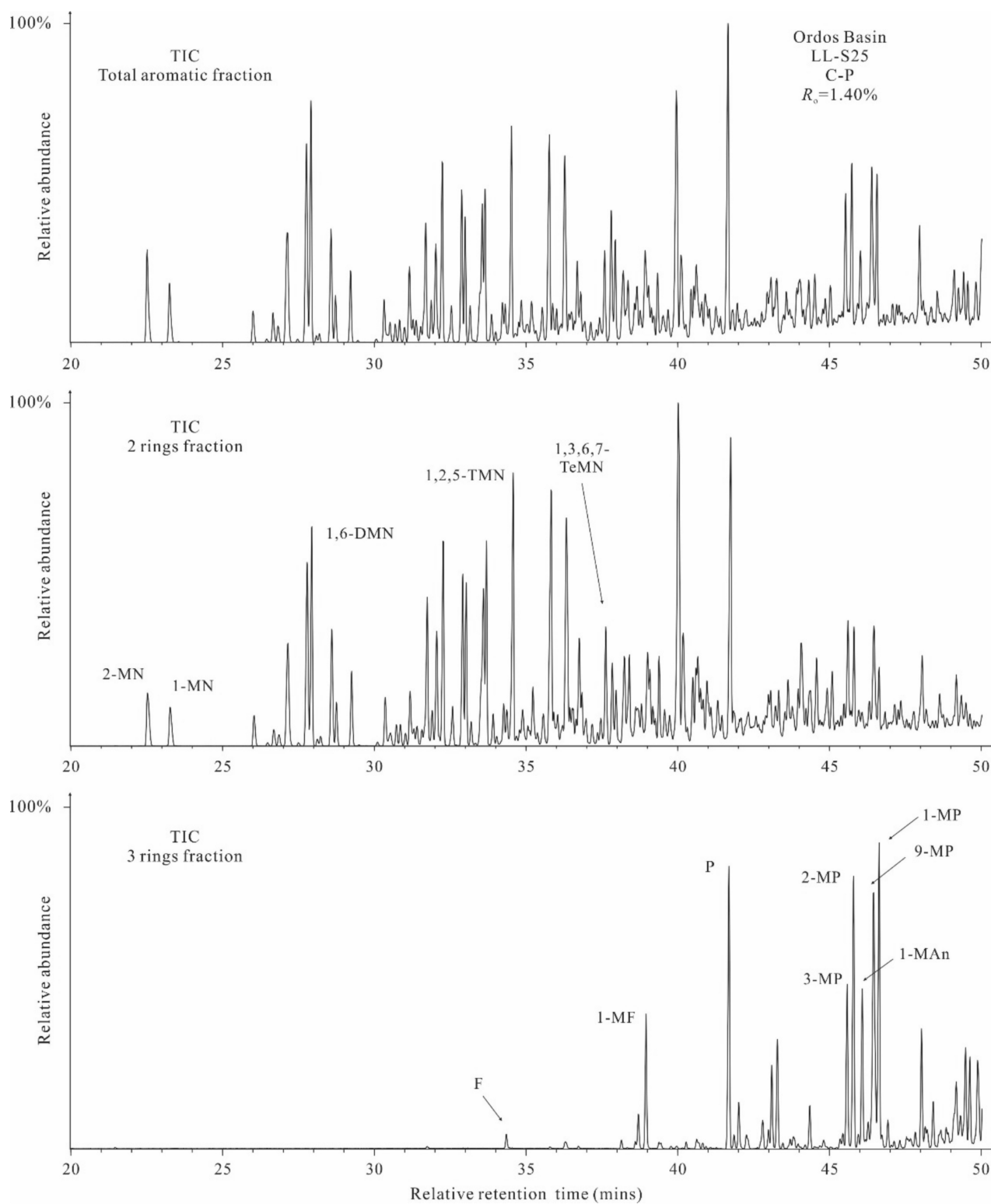


Fig. 3 Total ion chromatograms of two- and three-ring fractions separated from LL-S25 samples, representing the distribution of two- and three-ring aromatic hydrocarbons

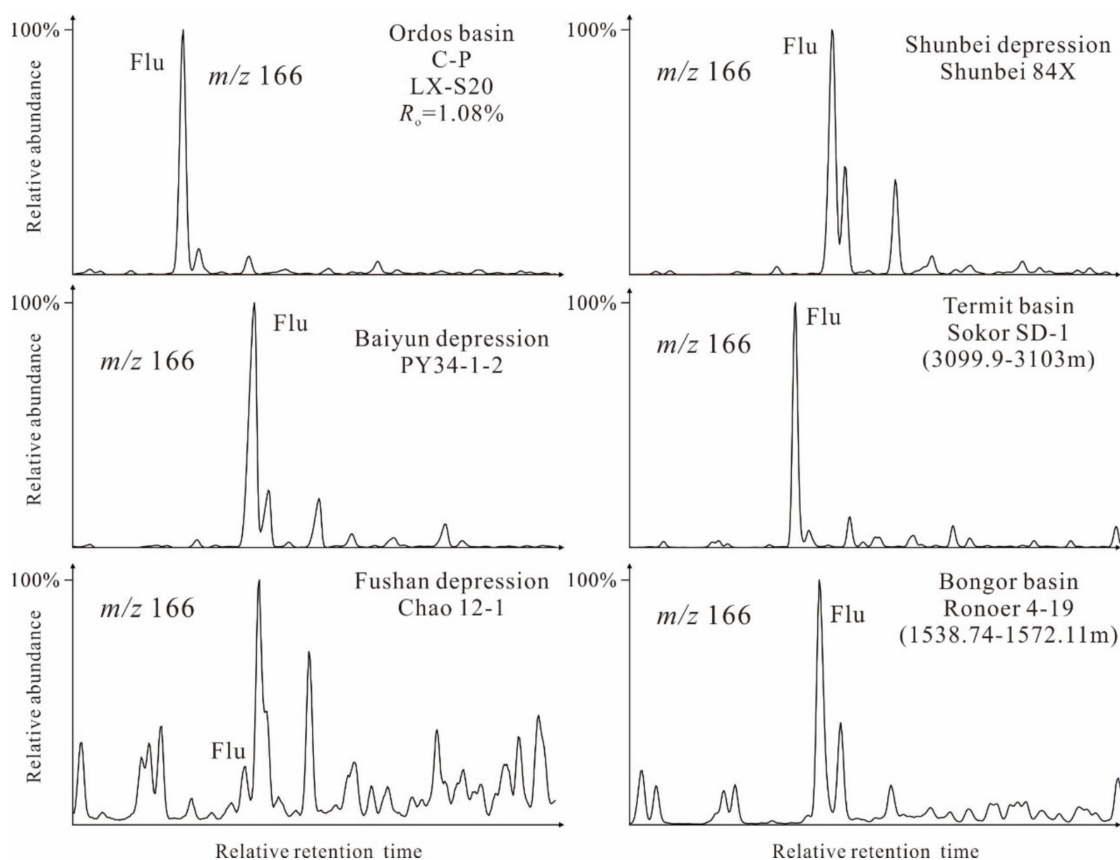


Fig. 4 Identification of fluorene (Flu) (m/z 166) in selected samples

Organic chemical analysis of plants has shown that Flu and MF structures containing natural products exist in many different organisms in various ecological environments, including *Taiwania cryptomerioides* (gymnosperms) (Lin et al. 1995), *Galanthus gracilis* (angiosperms), and *Dendrobium densiflorum* (grasses) in terrestrial environments (Zhang et al. 2007), *Terpios hoshinota* (spongy plants) in marine environments, and *Penicillium* (fungi) (Teruya et al. 2003; Shi and Guo 2016). Despite their petrogenic origins, a wide range of biological precursors still form the basis for the occurrence of Flu and 1-MF in various environmental sediments.

Previous studies of the $\delta^{13}\text{C}$ of sedimentary OM have indicated that the origin of OM is a crucial factor in determining the isotopic distribution of individual compounds (Galimov 2006; Buczyńska et al. 2013; Karp et al. 2020). $\delta^{13}\text{C}$ analyses of OM from plant fossils are an important tool for investigating the characteristics of climate changes and paleoecological adaptations (Murry et al. 1998; Forte et al. 2022), and the $\delta^{13}\text{C}$ of individual PACs associated with biological activity are often used to refine source and paleoenvironmental reconstructions (Buczyńska et al. 2013; Cesar and Grice 2017; Zakrzewski et al. 2024). Therefore, although the biological precursors of their

organic parent material cannot be accurately determined, it is considered that the differences in $\delta^{13}\text{C}$ for Flu and 1-MF in various sedimentary environments are probably associated with variations in their sources and sedimentary environments (Table 1; Fig. 6) and can therefore be useful tools for determining the heterogeneity and origins of OM. The high variability of $\delta^{13}\text{C}$ in the Flu and 1-MF in some samples (such as those from the Fushan Depression and Termit Basin) may represent higher diversity in OM sources (Fig. 6) (Karp et al. 2020; Forte et al. 2022; Zakrzewski et al. 2024).

The $\delta^{13}\text{C}$ values of Flu and 1-MF were obtained for various subclasses of the aromatic hydrocarbon fractions. The $\delta^{13}\text{C}$ values of selected aromatic hydrocarbons are shown in Table 1. The data in this study suggest that the $\delta^{13}\text{C}$ values of Flu and 1-MF isomers differ considerably among coals and crude oils from various depositional environments (Table 1). Samples from terrestrial depositional environments have markedly higher $\delta^{13}\text{C}$ values for Flu and 1-MF, but oils from marine depositional environments have lower $\delta^{13}\text{C}$ values for Flu and 1-MF than most of the other samples (Fig. 7). This is consistent with previous studies, which show that OM with mostly negative $\delta^{13}\text{C}$ values is probably derived from marine sources, whereas OM with higher $\delta^{13}\text{C}$ values

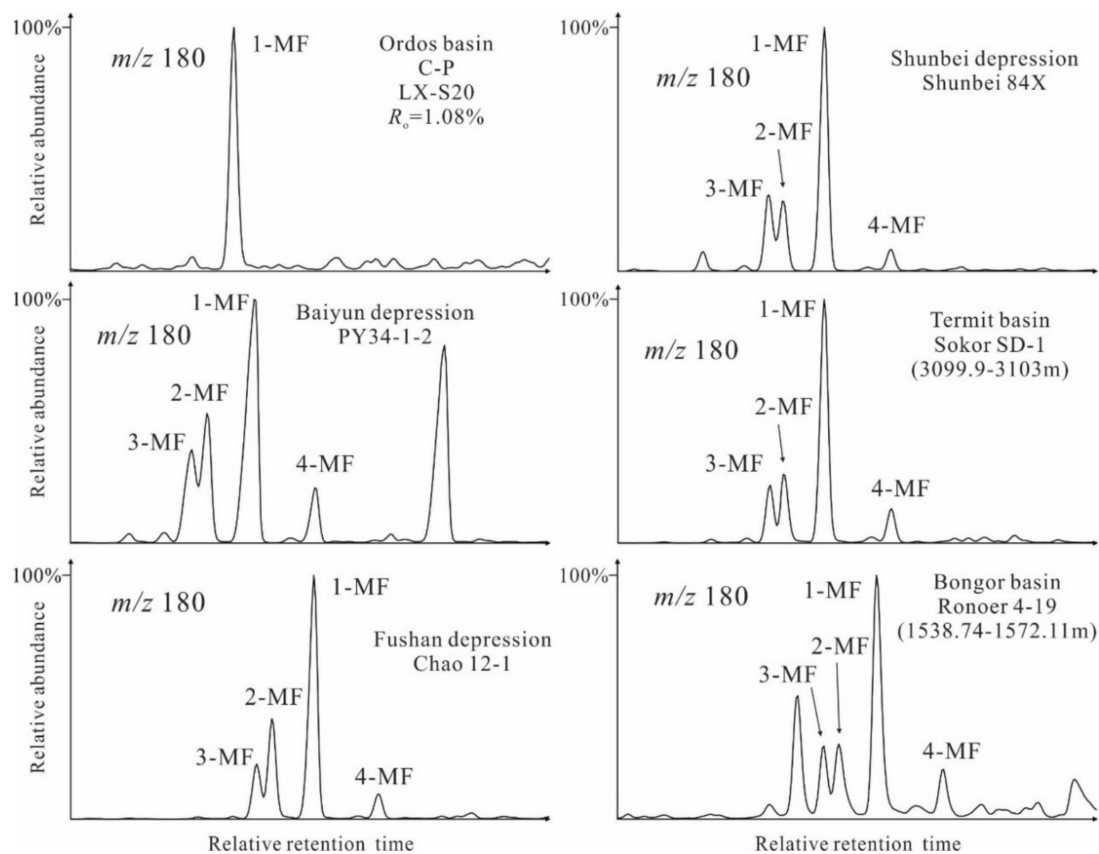


Fig. 5 Identification of isomers of methylfluorenes (MFs) (m/z 180) in selected samples

is representative of varying inputs of terrigenous material (Maslen et al. 2011; Cesar and Grice 2017; Niu et al. 2023).

The gradual changes in the $\delta^{13}\text{C}$ values of Flu and 1-MF with maturity are shown in Fig. 8. The thermal maturity of samples was assessed according to established maturity parameters, including MPI [(3+2)/(9+1)-MP] (Table 1). However, due to secondary alteration processes, MPI cannot be used for the oils from the Shunbei Depression, so in those cases, MNR (2/1-MN) was applied as a maturity indicator (Table 1).

Some studies have noted a general increase in the $\delta^{13}\text{C}$ of individual aromatic compounds with increasing thermal maturity (Le Métayer et al. 2014; Chen et al. 2016; Konan et al. 2022). However, this trend is not evident for the oils in this study (Fig. 8), indicating that there is little correlation between $\delta^{13}\text{C}$ values of Flu and 1-MF and thermal maturity.

It is worth noting that the samples with higher $\delta^{13}\text{C}$ values of Flu and 1-MF are derived from terrestrial depositional environments with greater input of higher plants, as compared to those from marine depositional environments with more aquatic input. These results indicate that the $\delta^{13}\text{C}$ values of Flu and 1-MF are potential geochemical indicators for distinguishing the depositional environments and sources of OM.

4.3 $\delta^{13}\text{C}$ of Flu and 1-MF is indicative of depositional environment and source of OM

Figure 9a and b show the cross plot of the DBT/Phen and (1+4)/(2+3)-MDBF ratios versus the Pr/Ph ratio for samples from various depositional environments (Radke et al. 2000; Yang et al. 2017). Crude oils derived from marine carbonate and fluvial/deltaic can be clearly distinguished (Zone 2 and Zone 5; Zone 1A and Zone 3). However, the present data suggest that these diagrams would need to be modified for crude oils from source rocks deposited in marine and transitional environments, as well as coals (Table 1; Fig. 9).

When plotted against Pr/Ph ratios, the $\delta^{13}\text{C}$ values for Flu and 1-MF are useful for investigating the effects of depositional environment and sources of OM in crude oils and sediments. The related data points for coal extracts and oils derived from various depositional environments fall in the cross-plot of $\delta^{13}\text{C}$ Flu and $\delta^{13}\text{C}$ 1-MF versus Pr/Ph (Fig. 10). The cross-plots can be divided into five zones, as shown in Fig. 10a and b. Each zone indicates a different depositional environment and OM source. Generally, samples from marine depositional environments with less terrigenous input have lower $\delta^{13}\text{C}$ values of Flu and 1-MF ($< -28\text{‰}$) than those from lacustrine depositional environments, and

Table 1 Compound-specific carbon isotope data and thermal maturity indicators for selected compounds in the oils and sediments derived from various depositional environments

Basin	Samples	$\delta^{13}\text{C}$ (‰, VPDB)		MPI	MNR	DBT/Phen	(4+1)/(2+3)-MDBFs	Pr/Ph
		Flu	1-MF					
Ordos Basin	PX-S22	−23.9	−24.6	0.47		0.08	1.24	2.17
	BD-S24	−24.0	−25.9	0.75		0.01	1.20	3.62
	XX-S10	−24.0	−25.5	0.72		0.01	1.99	2.89
	LX-S20	−23.6	−24.5	1.07		0.27	1.11	2.01
	LL-S25	−23.5	−25.0	0.74		0.01	1.20	2.23
Baiyun Sag	LH21-2-1	−29.0	−28.1	1.19		0.20	1.77	4.46
	PY34-1-2	−25.0	−26.6	1.48		0.08	1.67	4.40
	PY35-1-2	−26.1	−26.0	1.60		0.09	1.85	4.42
	PY 30-1-2	−27.6	−27.2	1.45		0.20	1.58	4.59
	LH 19-5-2	−27.9	−27.4	1.18		0.18	1.52	4.69
	LW 3-1-2	−26.3	−26.7	1.63		0.09	1.47	3.27
	LW 3-1-3	−25.7	−26.2	1.77		0.09	1.58	3.29
	LW 3-1-4	−27.5	−28.3	1.75		0.09	1.64	3.21
	LH 16-2-1		−27.5	0.91		0.21	1.75	3.73
	LH 23-1-1	−29.7	−26.0	1.20		0.19	1.94	3.84
	Fushan Depression Yong 8-6		−29.0	0.94		0.09	1.27	3.02
	Yong 8-7		−30.8	0.85		0.09	1.33	3.02
Fushan Depression	Yong 8-8		−30.1	0.93		0.10	1.26	3.30
	Yong 15-5		−29.7	0.88		0.09	1.18	3.13
	Yong 6-2		−29.6	0.98		0.10	1.26	3.02
	Yong 7-1	−24.8	−28.6	0.64		0.48	2.77	1.75
	Chao 12-1		−28.7	0.64		0.15	1.32	2.76
	Chao 22	−33.5	−27.8	0.76		0.08	1.11	2.62
	Chao 6-1	−27.3	−27.7	0.75		0.14	1.18	2.70
	Chao 7-1	−24.8	−28.6	0.63		0.14	2.80	1.72
	Hong 5-1	−29.5	−28.7	0.76		0.12	1.10	2.82
	Mei 5-9	−27.4	−27.6	0.50		0.16	1.83	2.66
	Mei 12	−28.9	−27.3	0.74		0.12	1.40	2.97
	Mei 4-1	−25.2	−28.0	0.74		0.10	1.01	2.93
	Mei 13	−28.1	−28.5	0.86		0.10	1.18	2.94
	Shunbei Oilfield Shunbei 41X	−27.3	−30.6		1.61	1.35	9.51	0.83
	Shunbei 43X	−32.6	−31.3		2.05	0.88	6.27	0.83
Shunbei Oilfield	Shunbei 44X	−28.7	−30.8		2.30	1.01	1.59	0.84
	Shunbei 701X	−30.9	−31.2		1.52	0.20	1.57	1.28
	Shunbei 84X	−30.0	−28.9		2.99	0.40	1.06	0.86
	Shunbei 21X	−33.1	−26.2		1.61	0.25	0.66	0.96
	Shunbei 4-1H	−29.9	−30.4		2.79	2.19	3.37	0.81
	Shunbei 6X	−28.8	−30.0		2.44	0.26	1.03	0.88
	Shunbei 82X	−32.0	−30.2		2.61	0.31	0.83	1.00
	Shunbei 8X	−31.0	−29.9		4.63	0.08	0.78	0.84
	Shunshen 1	−31.5	−29.7		3.44	0.18	0.93	0.99

Table 1 (continued)

Basin	Samples	$\delta^{13}\text{C}$ (‰, VPDB)		MPI	MNR	DBT/Phen	(4+1)/(2+3)-MDBFs	Pr/Ph
		Flu	1-MF					
Termit Basin	Sokor SD-1 (3245.6)	-22.6	-26.6	0.74		0.08	1.51	1.02
	Sokor SD-1 (3099.9)	-27.5	-26.5	0.73		0.08	1.52	1.01
	Yogou DST-1	-22.6	-26.3	0.74		0.08	2.00	1.06
	Yogou E-DST-3	-26.5	-26.3	0.53		0.00		0.83
	Goumeri-1 (E1)	-19.9	-24.5	0.57		0.07	1.73	0.93
	Goumeri-1	-18.9	-25.5	0.51		0.09	2.23	0.91
	Achigore (Deep-1)	-22.5	-26.9	0.64		0.09	2.09	0.93
	Bokora E-1	-22.4	-25.9	0.61		0.08	2.89	1.21
	Tairas S-1D (DST-3)	-20.4	-23.7	0.67		0.08	2.00	1.08
	Tairas S-1D	-21.6	-27.4	0.55		0.08	2.67	0.88
Bongor Basin	Raphia S-1 (811.7)	-26.9	-26.3	0.63		0.05	1.21	1.58
	Raphia S-1 (980.86)	-28.5	-25.4	0.65		0.05	2.02	1.53
	Raphia SW-2	-28.6	-27.1	0.76		0.05	2.49	1.54
	Mimosa-9	-28.3	-27.1	0.72		0.04	2.47	1.49
	Mimosa N-1	-32.0	-25.9	0.64		0.00	2.91	1.38
	Ronoer 4-19	-31.0	-26.7	0.65		0.07	1.61	1.71
	Baobab C1-15	-25.7	-27.1	0.70		0.03	2.04	1.76
	Baobab-1	-28.7	-28.4	0.42		0.05	2.32	1.76

Flu, fluorene; MF, methylfluorene; MP, methylphenanthrene; MN, methylnaphthalene; DBT, dibenzothio-
 phene; Phen, phenanthrene; MDBF, methyl dibenzofuran; Pr, pristane; Ph, phytane; MNR:2/1-methylnaph-
 thalene

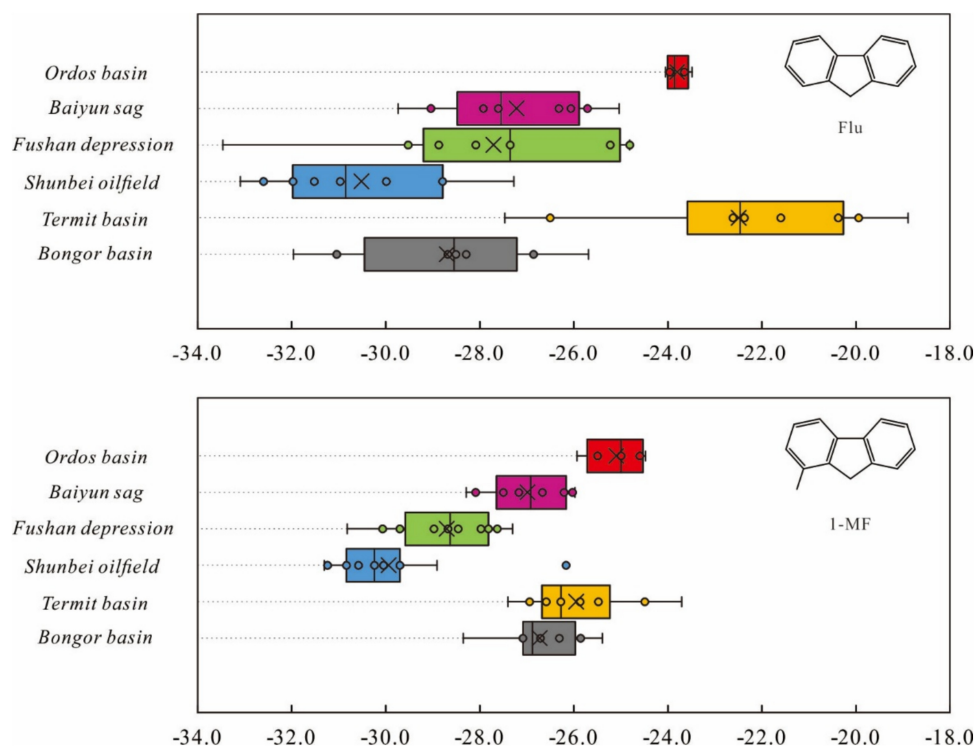
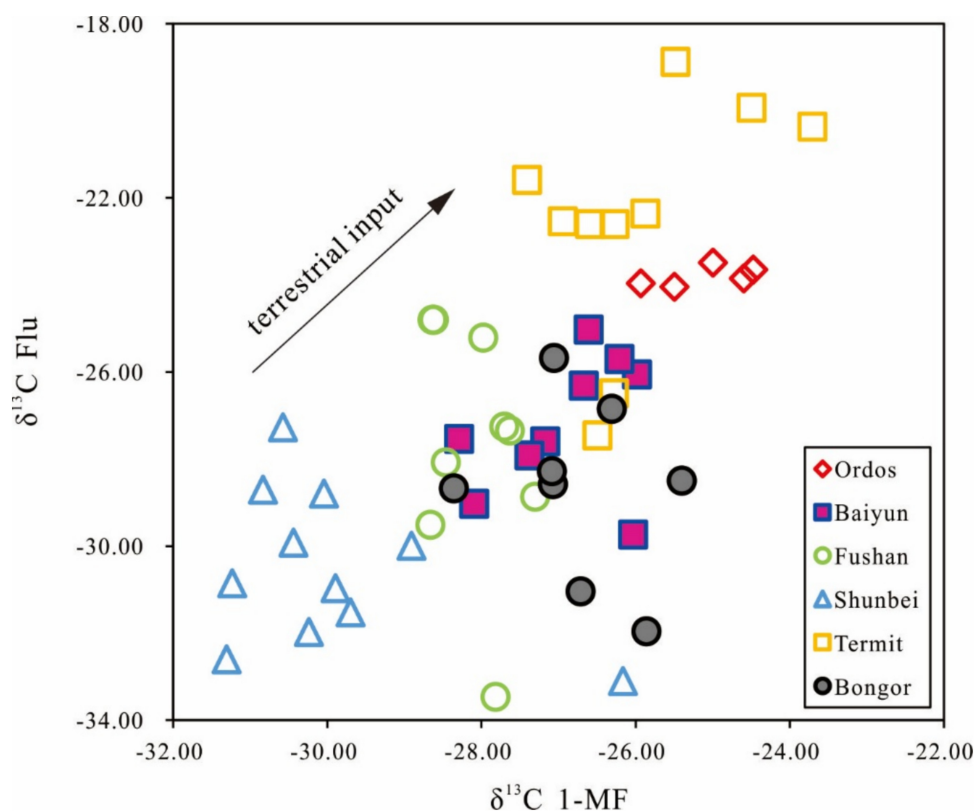
Fig. 6 Carbon isotope distributions of Flu and 1-MF from different sedimentary environments

Fig. 7 Cross-plot of the $\delta^{13}\text{C}$ values of Flu versus that of 1-MF for the crude oils and related sediments



all samples from typical coals with obviously higher plant input have $\delta^{13}\text{C}$ values of Flu and 1-MF $> -26\text{‰}$ and Pr/Ph ratios > 2 (Fig. 10) (Maslen et al. 2011). On the two diagrams, samples derived from various depositional environments are basically distinguishable (Fig. 10). In particular, samples derived from marine environments with algal input (Zone 1), terrigenous environments influenced by marine transgression (Zone 4), and deltaic/lacustrine/coastal facies (Zone 3) are distinguished from each other.

More work is needed to determine the origins and formation of Flu and MFs in oils and sediments. However, this study shows their potential application in depositional environments. Further laboratory experiments and case studies will expand the significance of these findings in organic geochemistry.

5 Conclusions

$\delta^{13}\text{C}$ values of Flu and its methylated homologues are suitable indicators for describing the original inputs of marine versus terrigenous OM during deposition. In this study, Flu and 1-MF were identified, and $\delta^{13}\text{C}$ values were obtained for subclasses of the aromatic fractions of crude oils and coals derived from various depositional environments. In general, the variations in $\delta^{13}\text{C}$ values may be related to the different sources of methylene in different depositional environments, as the samples derived from terrestrial facies have higher $\delta^{13}\text{C}$ values of Flu and 1-MF than those from marine facies. The $\delta^{13}\text{C}$ values of Flu and 1-MF, when coupled with the Pr/Ph ratio, provide useful ways to infer the depositional environments of sediments and related oils. These parameters are particularly applicable for distinguishing marine samples, deltaic/lacustrine/coastal samples, and transitional (mixed marine-terrestrial) samples that have been subjected to marine transgression and have similar depositional environments. This study provides new parameters for investigating the origins of organic sources in these and other oils and sedimentary OM.

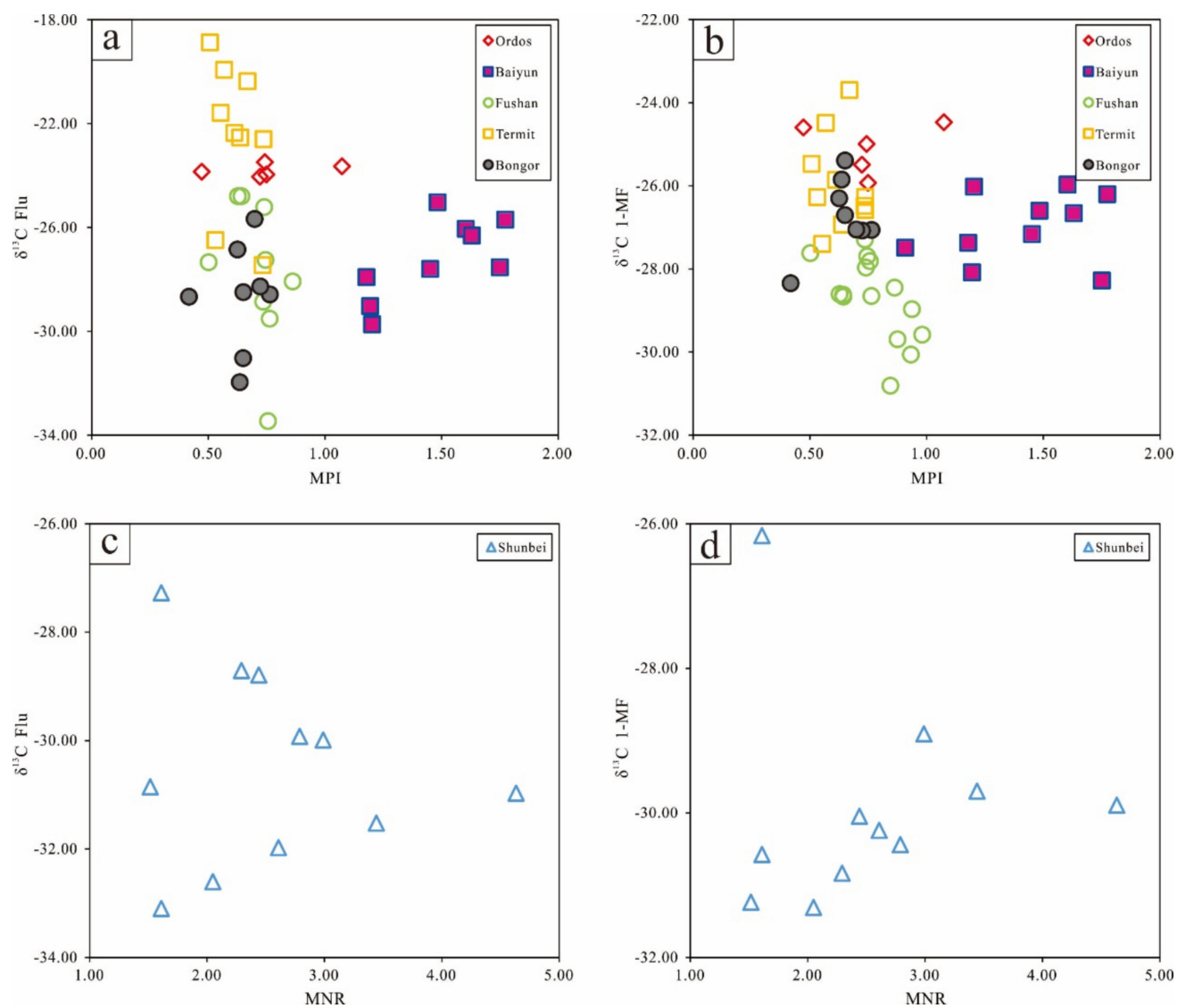


Fig. 8 Relationship between the $\delta^{13}\text{C}$ values of selected compounds and thermal maturity indicators in selected samples

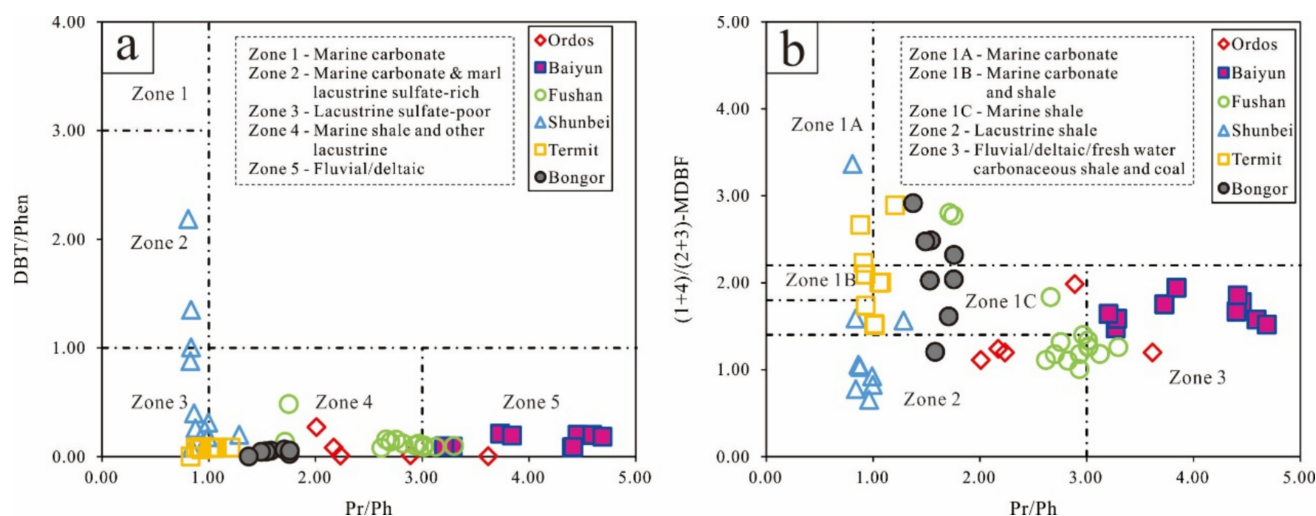


Fig. 9 Cross-plots of the **a** DBT/Phen ratio versus Pr/Ph (Radke et al. 2000) and **b** (1+4)/(2+3)-MDBF ratio versus Pr/Ph (Yang et al. 2017) showing the depositional environments of crude oils and sediments. Pr, pristane; Ph, phytane; Phen, phenanthrene; DBT, dibenzothiophene; MDBF, methylidibenzofuran

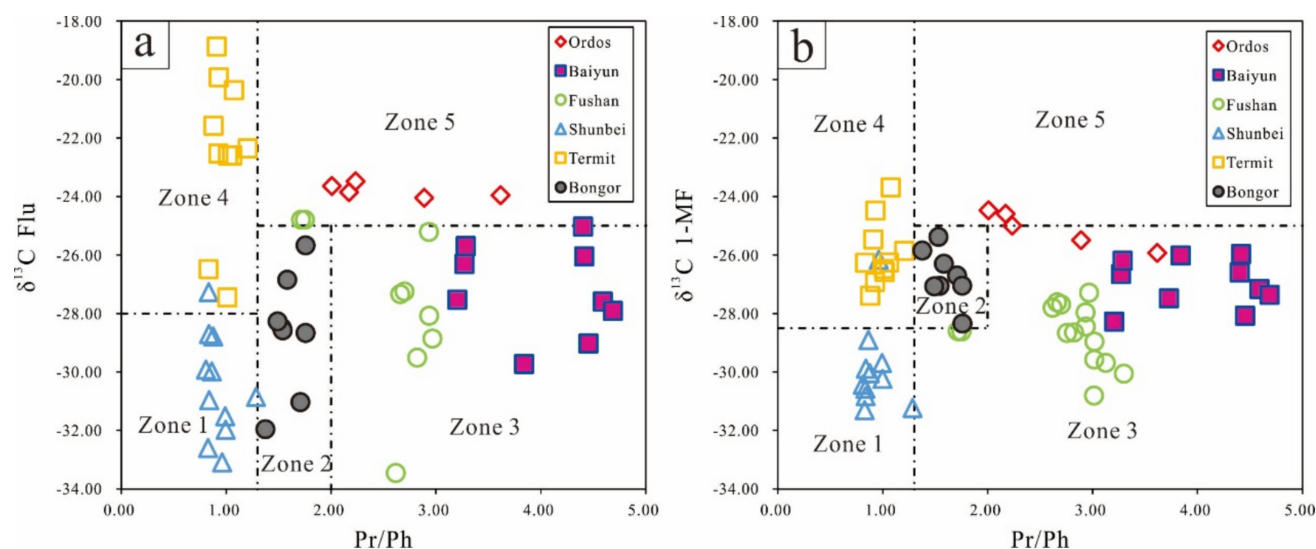


Fig. 10 Cross-plot of the $\delta^{13}\text{C}$ values of **a** Flu and **b** 1-MF versus the pristane/phytane ratio (Pr/Ph) showing the depositional environment of crude oils and sediments. Zone 1, Marine, algae; Zone 2, lacustrine, algae and bacterial mixed; Zone 3, fluvial/freshwater lacustrine/deltaic-coastal, aquatic and terrigenous mixed; Zone 4, terrigenous with influence of marine transgression, mixed and terrigenous-dominated; Zone 5, coal. Flu, fluorene; MF, methylfluorene

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Author contributions Ziao Geng, Meijun Li and Shuichang Zhang were responsible for the writing and revision of the manuscript;

Shengbao Shi, Lei Zhu, Tiantian Li and Jianfeng Zhang were responsible for the experimental instrumentation, software provision.

Declarations

Conflict of interest The authors declare that there is no conflict of interest regarding the publication of this paper.

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