Investigation of hydropyrolysis released aromatic hydrocarbons from Permian kerogens at different maturities in the Sichuan Basin, China

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ABSTRACT

Catalytic hydropyrolysis (HyPy) was used to release covalently bound aromatic hydrocarbons from both mature and overmature Permian source rocks in the Sichuan Basin, China. The released covalently bound aromatic hydrocarbons were discussed and compared with their free counterparts obtained by Soxhlet extraction. Furthermore, a mature Permian Dalong kerogen was selected for artificial simulation experiments. The HyPy experiments of the above thermal altered kerogens were subsequently conducted. The results from the artificial simulation sequence were also discussed and compared with those from the natural maturity sequence. For both natural maturity sequence and artificial simulation sequence, the distributions of covalently bound methylphenanthrenes and methyldibenzothiophenes are quite similar at different maturity stages. Triaromatic and monoaromatic steroids which are the aromatization products of steroids were not detected in covalently bound aromatics of all samples. The above results indicate that the rearrangement of methyl group on aromatic nucleus and the aromatization of steroids within kerogen was retarded to some extent or even prohibited, due to the protection of macromolecular structure below a vitrinite reflectance of 2.4%. It implies that aromatic maturity-related biomarker parameters based on the rearrangement and aromatization reactions within kerogens are probably not appropriate for maturity assessment. Meanwhile, perylene which is easily altered by thermal alteration was still existent in covalently bound aromatics released from the Dalong Formation even at over mature stage (Ro: 1.8%) and from the thermal altered kerogen until the temperature below of 400 °C (H/C: 0.49). It means the covalently bound perylene can be protected by macromolecular structure from the destruction of thermal stress at least below Ro of 1.8% (or H/C > 0.5). The results obtained also permitted the geochemical characterization of the source rocks.

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1. Introduction

Aromatic hydrocarbons refer to compounds containing the benzene ring structure and extensively exist in source rocks, crude oils and modern sediments. There are three kinds of geologic occurrence form for aromatic hydrocarbons: free, bound, and covalently bound states [1]. Free aromatic components are often present in crude oils or obtained by Soxhlet extraction from source rocks, which is the most widely used form in the research of petroleum geochemistry [2,3]. Bound aromatic hydrocarbons are compounds which physically included into the mineral inclusion or macromolecular structure, and are rarely reported because they are easily affected by medium environment (such as mineral composition).

Covalently bound aromatic hydrocarbons refer to those chemically incorporated into the macromolecular structure of kerogen or bitumen. They could be released by thermal cracking (pyrolysis) and/or chemical degradation from kerogens and bitumens [4–9]. Previously, numerous studies have focused on the origin, composition and distribution characteristics of free aromatic hydrocarbons, and on its applications in oil-source correlation, sedimentary environment, maturity evaluation and hydrocarbon migration [3,10–16].

Aromatic hydrocarbons in geologic samples are believed to be derived from two major processes: (1) early diagenesis and/or catagenetic alterations of biogenic precursor materials, and (2) high-temperature fragmentation (combustion) and/or recombination of organic matters [15,17–20]. With increasing thermal maturity, the stereochemical structures of the free aromatic hydrocarbons derived from biogenic process will be largely destroyed by thermal stress. Thus, thermal alteration often obscured the

original organic geochemical information of free aromatic hydrocarbons. Whereas, previous studies confirmed that the original organic geochemical information can still be preserved even at high-overmature maturity level in the covalently bound saturated biomarkers within the macromolecular structure of kerogens and/or bitumens [21,22]. There is no doubt that part of this information also can be preserved in the covalently bound aromatic biomarkers. It means that the covalently bound aromatics have great potential in the organic geochemistry study for high-over mature samples.

Catalytic hydropyrolysis (HyPy) refers to an open-system pyrolysis at high hydrogen pressures (>10 MPa) in the presence of a dispersed sulphided molybdenum catalyst [6]. Previous studies suggested that HyPy can efficiently release covalently bound saturate hydrocarbons from kerogens and bitumens without adversely affecting their stereochemistries [6–7,21,22]. Murray et al. [23] suggested that the high hydrogen pressure used in HyPy appears to suppress the potential ability of clay minerals to promote cracking and isomerization during pyrolysis. It seems that HyPy technique is an effective technique to research covalently bound aromatics within kerogens. So far, the reports on the covalently bound aromatics released by HyPy are rare. Brocks et al. [24] used HyPy to research the covalently bound aromatics from kerogens of Archean age from the Hamersley Formation of Western Australia. They suggested that the molecular and carbon isotopic compositions of covalently bound aromatic hydrocarbons are very similar to those of free aromatic hydrocarbons obtained by solvent extraction of the host rocks. Subsequently, Sonibare et al. [25] reported the distribution of maturity-related aromatics released from heavily biodegraded oil seeps by HyPy. The aromatics released by HyPy from the carbonaceous material within meteorites [26] and from archaeological charcoals [27] were also reported. However, they all did not provide the discussion on the influence of thermal maturation to the covalently bound aromatics which is of great importance for the application of covalently bound aromatic in petroleum geochemistry.

The objective of this study is to investigate the influence of thermal maturation to the covalently bound aromatics release by HyPy from kerogens of different maturities. The mainly investigated samples are the Permian Dalong Formation source rocks in both Guangyuan (mature) and Wangcang (over mature) areas. They have very similar depositional environment but quite different maturity [28–30]. Thus, they are very suitable materials for the research of the thermal evolution of the covalently bound aromatics. Additionally, one source rock from mature Dalong Formation was selected to artificially simulate the process of natural maturation using anhydrous pyrolysis. The results from artificial maturity sequence were also discussed and compared with the above natural maturity sequence. Further, the possible applications of covalently bound aromatics within kerogens at high-over mature stage were discussed. This study would extend the application range of aromatic hydrocarbons to high maturity stage.

2. Methods and materials

2.1. Samples

The investigated samples are all selected from outcrops of Permian strata in the Sichuan Basin (shown in Fig. 1). In Permian strata, there are 4 major source rocks existing in the Sichuan Basin, the Longtan Formation, the Wujiaping Formation, the Changxin Formation and the Dalong Formation. Those Formations have different deposition environments. The Longtan Formation, consisting mainly of mudstone with small amount of coal, was deposited in paralic environment. The Wujiaping Formation and the Changxing Formation were deposited in marine environments [31]. The Dalong Formations were interbedded marine dark silicalites and mudstones, and mainly occur in the Guangyuan–Wangcang trough and the Western Hubei–Chengkou trough [28–30].

The total organic carbon (TOC), Rock-Eval data of the source rocks, bulk δ^{13}C values of kerogens, and the H/C atom ratios are presented in Table 1. TOC contents of all samples are over 2%. All

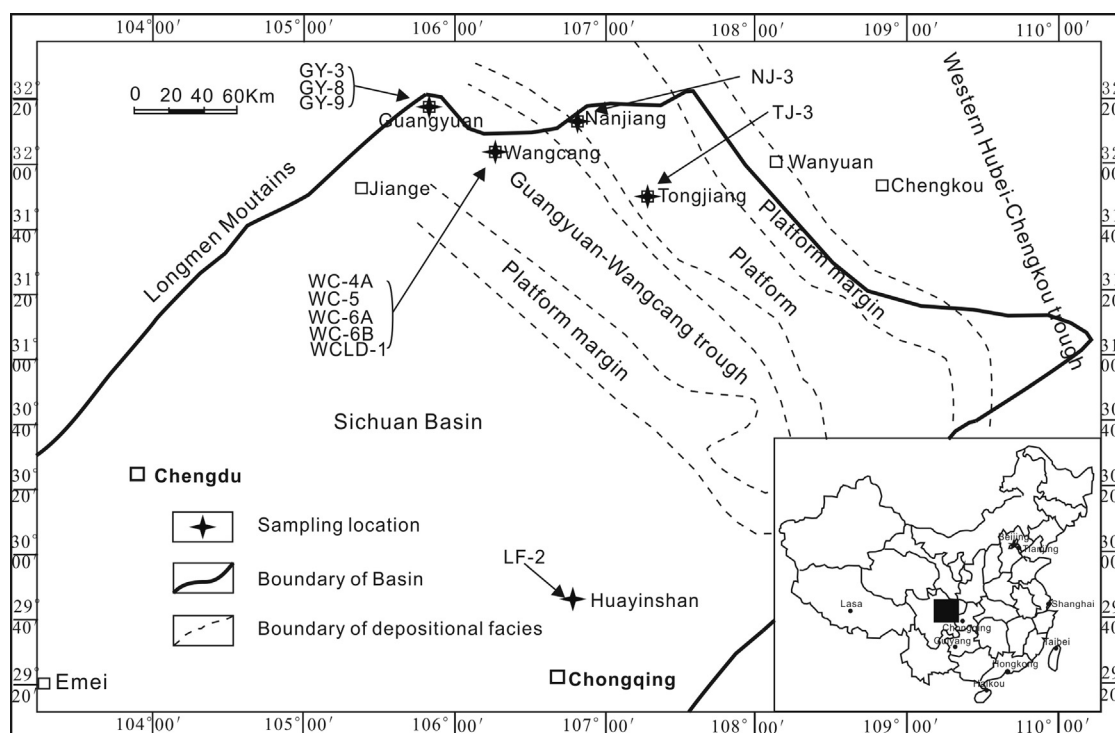**Fig. 1.** The geological map of sampling location.

Table 1
The basic information of the source rocks.

Sample ID	Formation	Lithology	$\delta^{13}C$ (‰)	Ro (%)	TOC (%)	S1	S2	Tmax(°C)	HI	H/C
GY-3	Dalong	Mudstone	−28.4	–	3.54	0.43	7.29	437	206	0.89
GY-8♦	Dalong	Silicalite	−27.6	0.6	8.75	1.22	30.06	438	343	0.87
GY-9♦	Dalong	Siliceous mudstone	−27.1	–	4.58	0.48	12.68	436	300	0.88
WC-4A♦	Dalong	Silicalite	−28.1	–	2.81	0	0.1	603	5	0.53
WC-5♦	Dalong	Mudstone	−27.5	1.8	4.07	0.04	0.18	601	5	0.55
WC-6A♦	Dalong	Silicalite	−27.1	–	8.54	0.01	0.15	552	2	0.54
WC-6B♦	Dalong	Mudstone	−27.3	–	7.1	0	0.15	556	2	0.55
NJ-3	Wujiaping	Mudstone	−26.2	1.9	8.39	0.04	0.21	604	2	0.48
TJ-3	Changxin	Limestone	−29.2	2.4	4.19	0.05	0.03	605	1	0.45
WCLD-1	Changxin	Mudstone	−28.8		6.07	0	0.07	542	1	0.46
LF-2	Longtan	Mudstone	−23.3	1.6	11.2	0.06	2.82	515	25	0.59

Note: ♦ Cited from Wu et al. [22].

investigated samples except the Dalong Formation of Guangyuan areas are over mature with *T*-max temperatures over 500 °C. *T*-max values of the Dalong Formation source rocks of Guangyuan areas range from 436 °C to 438 °C, implying that the samples are at the beginning of oil generation. The bulk kerogen $\delta^{13}C$ values of the Dalong Formations from both Wangcang and the Guangyuan outcrop sections are very similar, both in the range of −27.1‰ to −28.4‰ (Table 1). They have very similar depositional environments, but different maturities. The measured vitrinite reflectance (Ro) is 0.6% for GY-8, and 1.8% for WC-5. The Dalong Formation source rocks were sampled chronologically from old to young strata on the Guangyuan and Wangcang outcrop sections, with intervals from 0.2 m to 0.5 m. Thus, the maturities of source rocks from the same outcrop section should be quite similar. Ro values of the Wujiaping Formation (NJ-3, TJ-3) are in the range of 1.9–2.4%.

2.2. Kerogen preparation

The source rock samples were crushed to 80 mesh and then extracted with a mixture of DCM and methanol (93:7, v/v) at 46 °C for 72 h. Powered rock samples, then, were treated with acid to obtain kerogens. The 3 M hydrochloric acid (HCl) were used for removal of carbonate mineral, and the mixed solvent of hydrofluoric acid (HF) and 1 M HCl (v:v = 1:1) was used for removal of silicate mineral. At last, the kerogens were washed by distilled water to remove acids and dried at 60 °C in vacuum oven.

2.3. Artificial thermal alteration experiments

The kerogen of GY-8 was selected for anhydrous pyrolysis. Aliquots (0.6 g) of the five extracted kerogens were sealed in glass tubes under the protection of nitrogen gas. The tubes were then heated for 72 h at 350 °C, 380 °C, 400 °C, 430 °C and 460 °C, respectively. The calculated vitrinite reflectance (Ro) by Easy % Ro method [32] for the kerogens heated at 350 °C, 380 °C, 400 °C, 430 °C and 460 °C were 1.08%, 1.49%, 1.74%, 2.27% and 2.86%, respectively. After each thermal simulation, the pyrolysis product was recovered by repeated dichloromethane (DCM) sonication.

2.4. Kerogen HyPy experiment

All the kerogen samples (0.3–0.8 g) for HyPy were soxhlet extracted by ternary solvent (benzene/acetone/methanol = 5:5:2) for 2 weeks to remove soluble organic matter. HyPy apparatus has been previously described by Love et al. [6]. The solvent-extracted kerogens were impregnated with an aqueous solution of ammonium dioxydithiomolybdate [$(NH_4)_2MoO_2S_2$] to give a nominal loading of molybdenum of 5 wt%. Then, kerogen powders with catalyst were loaded into stainless steel reactor for HyPy using a hydrogen pressure of 15.0 MPa. A hydrogen flow of 4 L/min, measured at ambient temperature and pressure, was used through

the reactor. The kerogen powder was then vacuum-dried for subsequent HyPy experiment. HyPy experiment involves two steps, both steps were conducted in the same hydrogen pressure and hydrogen flow. At first, the sample was pyrolyzed with resistive heating from ambient temperature programmed to 300 °C (5 min) at 250 °C/min rate, to completely remove the adsorbed hydrocarbons and the weaker covalent bonds leaving the stronger bonds for HyPy. After all of the weaker covalently bound compounds were removed from the kerogen, the silica within the collecting tube was replaced [33]. The second heating run was employed from ambient temperature programmed to 250 °C at 300 °C/min rate, then increase to 520 °C at 8 °C/min rate, and finally kept at 520 °C for 5 min. Details of HyPy experiments can be referred to Wu et al. [22].

2.5. Instrumental

Analysis of aromatic hydrocarbons was conducted using a Thermo Scientific Trace GC ultra gas chromatography coupled to a Thermo Scientific Trace DSQ II mass spectrometer. A DB-1 fused silica capillary column (60 m 0.32 mm i.d. × 0.25 μm film thickness) was used. The GC oven was held isothermally at 70 °C for 2 min, programmed to 140 °C at 6 °C/min rate, and then to 290 °C at 3 °C/min rate with a final holding time of 25 min. Helium was used as carrier gas with a constant flow rate of 1.5 mL/min. The ion-source temperature was 250 °C, and the temperature of the injector was 290 °C. The ion source was operated in the electron impact (EI) mode with electron energy of 70 eV.

3. Results and discussion

3.1. Natural maturity sequence

Fig. 2 shows the distributions of aromatic hydrocarbons in the Soxhlet extracts from Permian source rocks and their corresponding HyPy products (hydropyrolysates). Abundant aromatic compounds existed in the Soxhlet extracts of source rocks, such as phenanthrene and benzothiophene. The naphthalene homologues were only abundant in the Dalong Formation from Guangyuan areas which are mature samples. The relative concentrations of naphthalene homologues in other overmature samples including the Dalong Formation from Wangcang areas were very low. It seems that the different distribution of free aromatics should be contributed to the influence of maturation. The influence of water washing also should not be excluded since they are all outcrop samples. However, covalently bound aromatic hydrocarbons in the source rocks of the same Formation were very similar. It implied that the covalently bound aromatic hydrocarbons were little influenced by the secondary alterations such as maturation, biodegradation and water washing.

Table 2
The maturity related aromatic parameters in both free and covalently bound hydrocarbons of Permian source rocks in Sichuan Basin and artificial simulation products of kerogen GY-8.

Sample ID	Simulation temp (°C)	Ro/easy Ro (%)	H/C	Free phase		Covalently bound phase	
				MPI-3	MDR	MPI-3	MDR
			Natural maturity sequence				
GY-8	–	0.6	0.87	0.37	2.1	0.64	11.64
LF-2	–	1.6	0.59	0.84	46.49	0.79	–
WC-5	–	1.8	0.55	0.77	21.24	0.75	–
NJ-3	–	1.9	0.48	0.67	17.4	0.76	–
WCLD-1	–	2.4	0.45	0.76	28.21	0.72	–
			Artificial simulation sequence				
GY-350	350	1.08	0.53	0.64	2.42	0.71	11.64
GY-380	380	1.49	0.49	0.74	3.09	0.74	11.2
GY-400	400	1.74	0.46	0.86	11.55	0.77	11.02
GY-430	430	2.27	0.37	0.71	10.42	0.8	11.3
GY-460	460	2.86	0.34	0.63	8.98	0.71	–

Note: "–" means no existence.

3.1.1. Naphthalenes, phenanthrenes and dibenzothiophenes

The distributions of methylated naphthalenes, phenanthrenes and dibenzothiophenes in free hydrocarbons were largely controlled by maturation [34–37]. With the increasing maturity, the less stable substituted isomers (α-substitution pattern) will transfer into more stable ones (β-substitution pattern) by rearrangement reaction, such as 9-MP to 3-MP and 1-MDBT to 4-MDBT [34]. Thus, the predominance of 2-MP and 3-MP over 1-MP and 9-MP is used as maturity parameters such as MPI-3 ([3-MP+2-MP]/[1-MP+9-MP]) [34]. The MDR ratio (4-MDBP/1-MDBP) was also reported by Radke et al. [38] as a maturity parameter.

Fig. 3 shows representative expanded mass chromatograms of the naphthalenes, phenanthrenes and dibenzothiophenes in free aromatics with compound identifications given in Table 3. The 9-methylphenanthrene (9-MP) and 1-MP are predominant compounds in GY-8, but their relative abundance are reduced in other overmature samples (Fig. 3). Additionally, the relative concentration of 1-methyldibenzothiophene (1-MDBT) in GY-8 was also higher than other samples. The MPI-3 ratio and MDR ratio are 0.37 and 2.10, respectively, for the GY-8 (Ro: 0.6%). For other overmature samples, the MPI-3 ratio and MDR ratio are both higher than those for GY-8 (Fig. 3 and Table 2). However, they are not monotonically increased with the maturity (Fig. 3). The MPI-3 ratio and MDR ratio for LF-2 are both higher than those for WC-5, although the maturity of the latter is higher than that of the former. Previous studies also suggested that the relative distribution of MP can be affected by the type and origin of organic matter [39,40]. Thus, the fluctuation of MPI-3 ratio and MDR ratio could be attributed to the facies variation.

However, covalently bound aromatics for all investigated samples display a very similar distribution of methylphenanthrenes and methyldibenzothiophenes (Fig. 4). The relative concentrations of α-substituted methylphenanthrenes (9-MP and 1-MP) were all lower than β-substituted isomers (3-MP and 2-MP). The 1-MDBT was found in very small amounts in all samples. Those observations should be the characteristics of high and over mature sources, but also occurred in the covalently bound aromatics of mature samples (GY-8). Though the MPI-3 ratio of GY-8 (0.64) is still lower than other overmature samples (on the range of 0.72–0.79). Thus, the distributions of methylphenanthrenes in the hydropyrolysates cannot be explained as the results of maturation, but probably were the original distribution characteristics within kerogen .

Both isomerization and demethylation reaction will influence the MP distribution. The work by Marke et al. [41] pointed out that the differences between energy barriers for the ionic demethylation of the MP isomers (approximately 3 kcal/mol) are much lower than those of the isomerization reactions (7.4–24.9 kcal/mol). It

Table 3
Peak identifications in the naphthalenes, phenanthrenes and dibenzothiophenes mass fragmentograms.

Peak no.	Compound name
	Naphthalenes
a	2-Methylnaphthalene
b	1- Methylnaphthalene
c	2-Ethylnaphthalene
d	1-Ethylnaphthalene
e	2,6 + 2,7-Dimethylnaphthalene
f	1,3 + 1,7-Dimethylnaphthalene
g	1,6-Dimethylnaphthalene
h	1,4 + 2,3-Dimethylnaphthalene
i	1,5-Dimethylnaphthalene
j	1,2-Dimethylnaphthalene
k	1,3,7-Trimethylnaphthalene
l	1,3,6-Trimethylnaphthalene
m	1,3,5 + 1,4,6-Trimethylnaphthalene
n	2,3,6-Trimethylnaphthalene
o	1,2,4-Trimethylnaphthalene
p	1,2,5-Trimethylnaphthalene
	Phenanthrenes
a	Phenanthrene
b	3-Methylphenanthrene
c	2-Methylphenanthrene
d	9-Methylphenanthrene
e	1-Methylphenanthrene
f	2,6 + 3,5-Dimethylphenanthrene
g	2,7-Dimethylphenanthrene
h	1,3 + 2,10 + 3,10 + 3,9-Dimethylphenanthrene
i	1,6-Dimethylphenanthrene
j	1,7-Dimethylphenanthrene
k	2,3-Dimethylphenanthrene
l	1,9-Dimethylphenanthrene
	Dibenzothiophenes
a	Dibenzothiophene
b	4-Methyldibenzothiophene
c	3,2-Methyldibenzothiophene
d	1-Methyldibenzothiophene
e	4-Ethyldibenzothiophene
f	4,6-Dimethyldibenzothiophene
g	2,4-Dimethyldibenzothiophene
h	1,4-Dimethyldibenzothiophene

Table 4
Peak identifications in the *m/z* 231 mass fragmentograms.

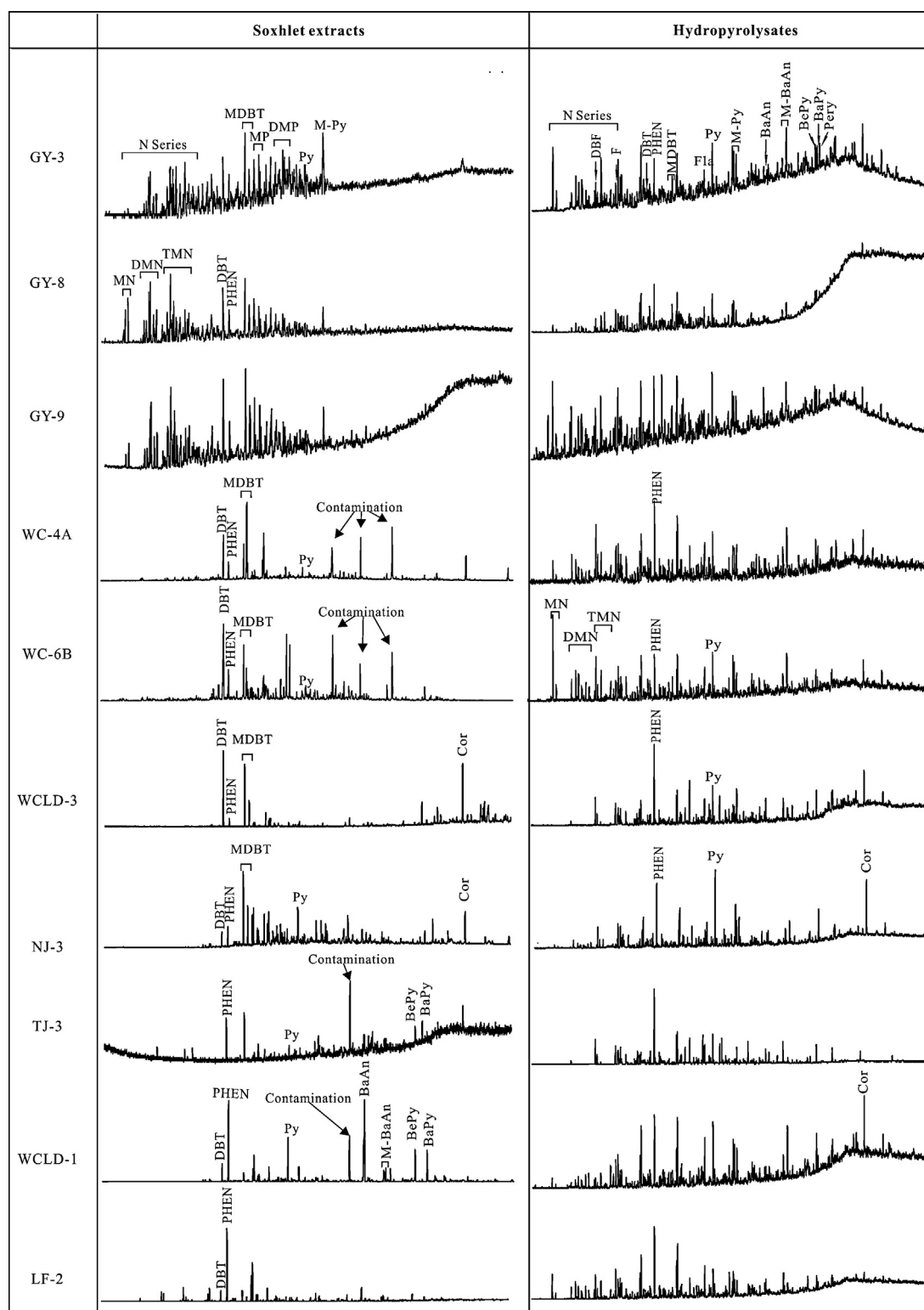| Peak no.	Compound name
a	C_{20} Triaromatic sterane
b	C_{21} Triaromatic sterane
c	C_{26} Triaromatic sterane (20S)
d	C_{26} Triaromatic sterane (20R) + C_{27} triaromatic sterane (20S)
e	C_{28} Triaromatic sterane (20S)
f	C_{27} Triaromatic sterane (20R)
g	C_{28} Triaromatic sterane (20R)

Fig. 2. TIC chromatograms of aromatic hydrocarbons in soxhlet extraction (free state) and hydropyrolysates (covalently bound state) from Permian source rocks.
Note: MN – methylnaphthalene; DMN – dimethylnaphthalene; TMN – trimethylnaphthalene; DBT – dibenzothiophene; PHEN – phenanthrene; MDBT – methyldibenzoth-iophene; MP – methylphenanthrene; DMP – dimethylphenanthrene; DBF – dibenzofuran; F – fluorene; Fla – fluoranthene; Py – pyrene; M-Py – methyl-pyrene; BaAn – benzo(a) anthracene; M-BaAn – methyl-benzo(a) anthracene; BePy – benzo(e) pyrene; BaPy – benzo(a) pyrene; Pery – perylene; Cor – coronene.

means the influence of cracking on the MP distribution is very small. Furthermore, the influence of HyPy technique on it released biomarkers is very small because of the use of high pressure hydrogen and the short residence time of hydropyrolysate in the hot pyrolysis tube [21,22]. Thus, the MP distribution for both free and covalently bound form is more likely influenced directly by isomerization [41,42]. In this study, the distributions of methylated phenanthrenes and dibenzothiophenes are changed with increasing maturity in free phase but are very stable in covalently bound phase. It implied that the rearrangement of methyl group
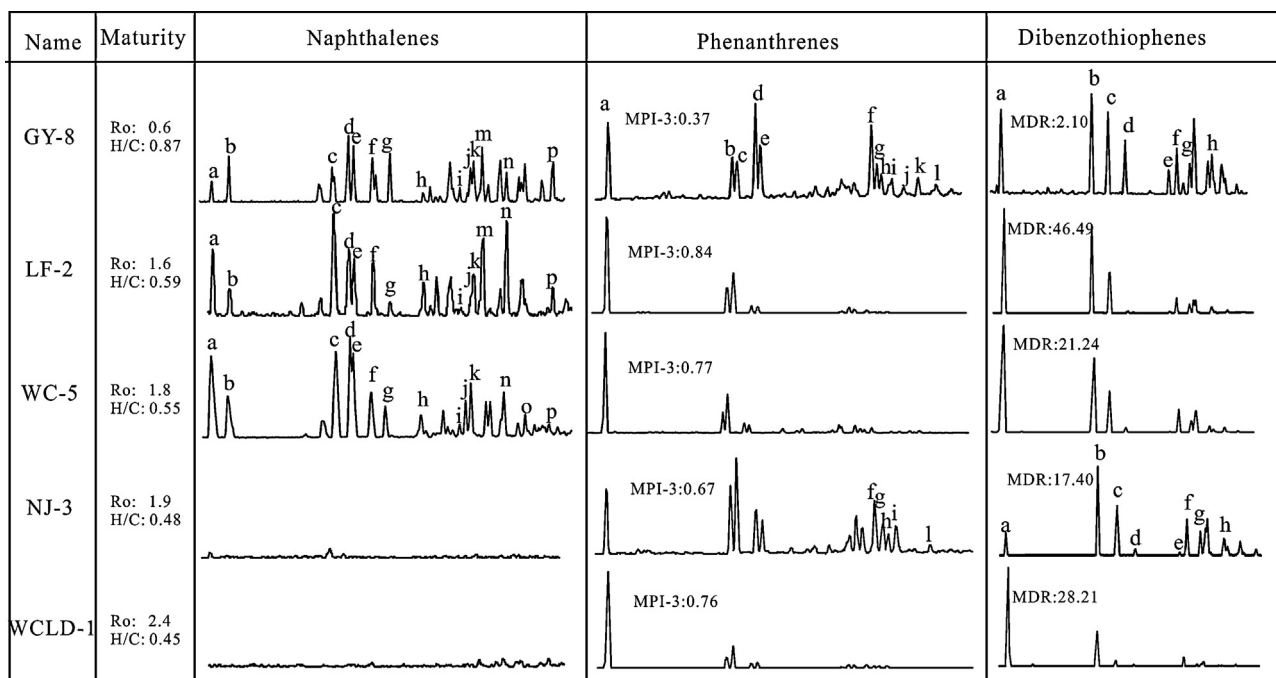
Fig. 3. Representative partial expanded gas chromatograms–mass spectrometry of the free aromatic fractions in natural maturity sequence with peak identifications in Table 3. Naphthalenes (*m/z* 142,156 and 170), phenanthrenes (*m/z* 178, 192 and 206), dibenzothiophenes (*m/z* 184, 198 and 206).
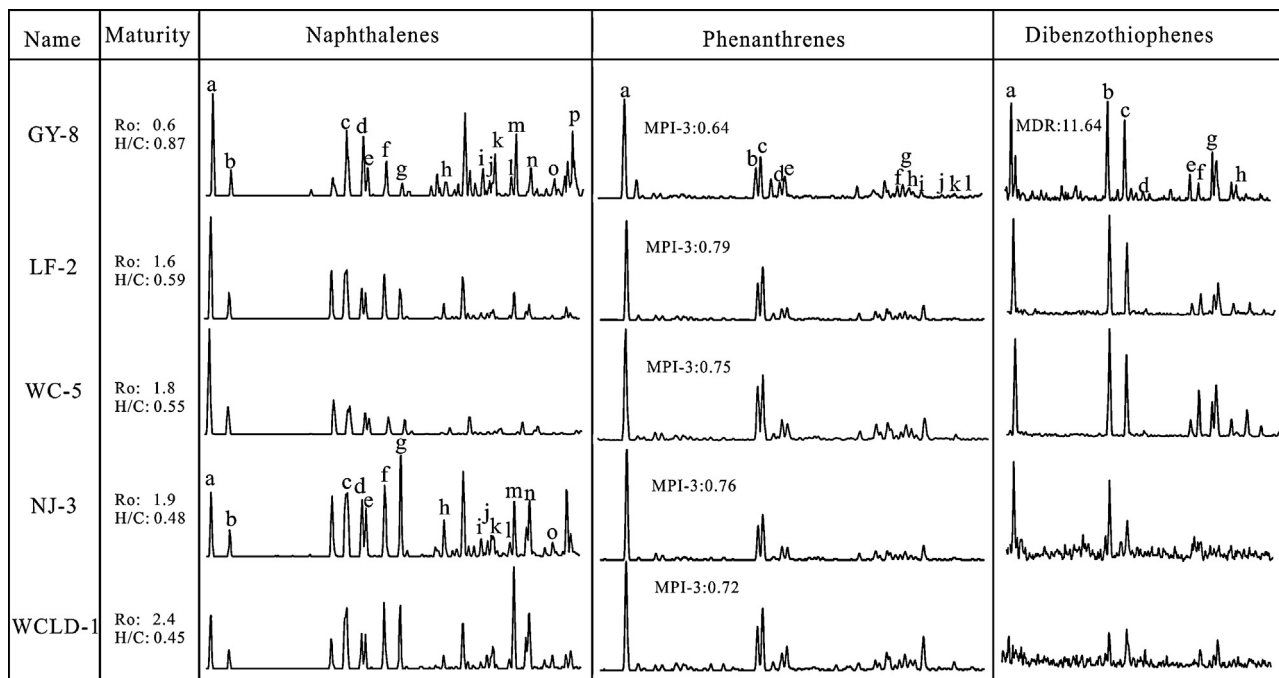

Fig. 4. Representative partial expanded gas chromatograms–mass spectrometry of the covalently bound aromatic fractions in natural maturity sequence with peak identifications in Table 3.

on the aromatic nucleus should be suppressed by the protection of kerogen macromolecular structure. Previous studies also have suggested that the rearrangement can be retarded in bound phase compared to free phase [23,43,44]. Murray et al. [23] reported that diasteranes which are the rearrangement products of regular steranes were observed at considerably less concentrations in the hydropyrolysates compared to the corresponding DCM extracts. The Ts (C$_{27}$ 17α-trisnorhopane), as the rearrangement product of

Tm (C$_{27}$ 18α-trisnorhopane), were also reported to be absent in the hydropyrolysates [43,44].

3.1.2. Aromatic steroids

Triaromatic steroids were identified in free aromatics obtained from the Dalong Formation source rocks, but the distributions and relative concentration of triaromatic steroids are different between the Guangyuan and the Wangcang areas (Fig. 5). Triaro-
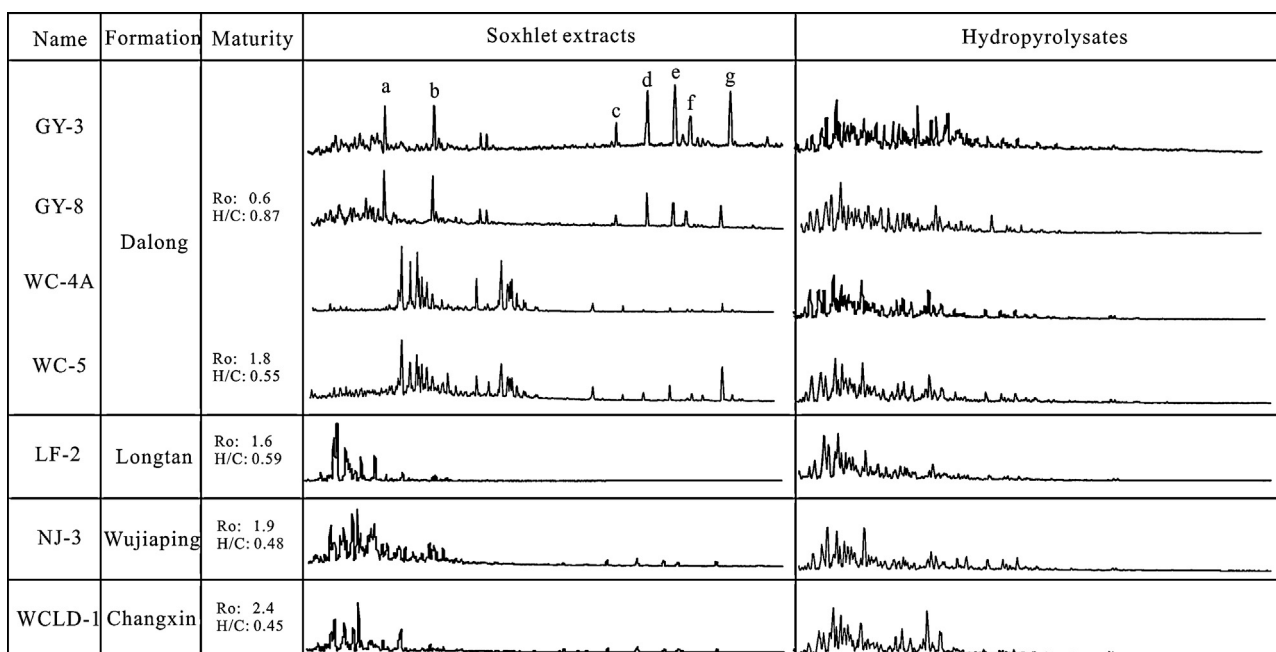
Fig. 5. Triaromatic (*m/z* 231) distribution of aromatic hydrocarbons obtained by soxhlet extraction and by HyPy in natural maturity sequence. Labeled peaks are identified in Table 4.
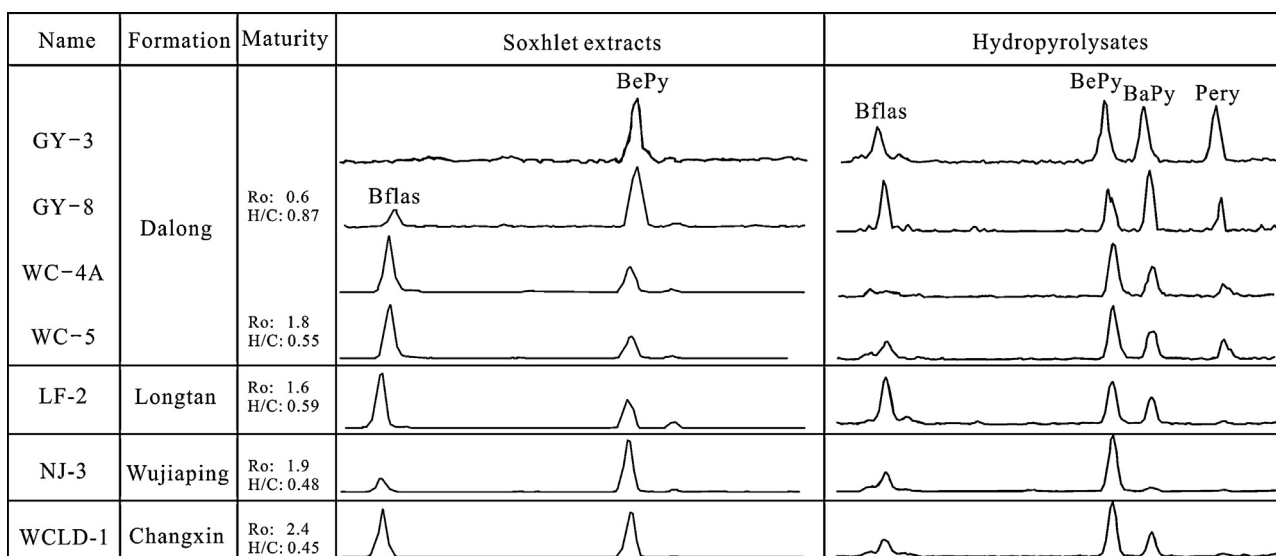

Fig. 6. The *m/z* 252 gas chromatograms–mass spectrometry of aromatic hydrocarbons obtained by soxhlet extraction and by HyPy in natural maturity sequence.

matic steroids also can be detected in NJ-3 and WCLD-1, but absent in LF-2. The difference of relative concentration of free triaromatic should be controlled by maturity and source [45,46]. However, tri-aromatic steroids and monoaromatic steroids were not detected in covalently bound aromatics of all samples.

It is widely accepted that monoaromatic and triaromatic steroids are the aromatization products of free steroids at the early stage of hydrocarbon generation [45–47]. The intact steroid skeletons are certainly present in kerogen, since covalently bound regular steranes were indeed detected in the Dalong Formation from both Guangyuan and Wangcang areas [22]. The absence of aromatic steroids in mature source rocks from Guangyuan areas probably means that the covalently bound steroids were not converted into aromatic steranes. With maturity increasing, the aromatization reaction will finally occur in kerogen. However, the covalently bound aromatic steroids are still not detected in the

overmature source rocks from Wangcang areas. Thus, we specu-late that the side chain of covalently bound steroid will be cracked before the aromatization. Therefore, aromatic steranes cannot be detected in the covalently bound hydrocarbons, since the biogenic carbon skeletons of covalently bound steranes were destroyed before aromatization reaction.

Actually, this phenomenon has been found previously. The aro-matic steroidal hydrocarbons has been detected in source rock heating experiments (heating 6–91 days), but absent in laboratory pyrolysis (heating 5 min) [48]. The latter is a reaction system that the products are removed immediately from the reaction site after generation, as HyPy technique used in this study. They suggested that the aromatization of steroids is occurring after generation [49]. It also implied that the cracking reaction occur easier than the aromatization reaction within kerogen. Meanwhile, the long residence time of kerogen heating experiments will aromatized
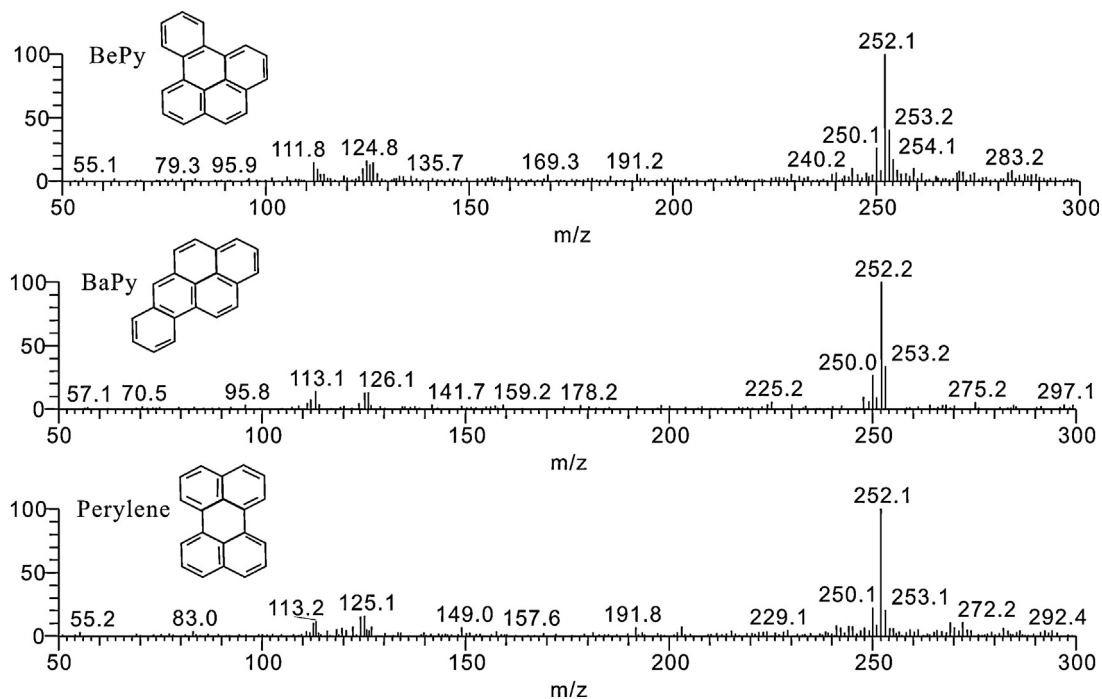
Fig. 7. Mass spectra of BePy, BaPy and Perylene in their elution sequence on Fig. 6.

the new generated steroids into aromatic steroidal hydrocarbons. Whereas, the short residence time of HyPy and laboratory pyrolysis will not allow the aromatization of products.

3.1.3. Perylene

Fig. 6 shows m/z 252 chromatographs of both free aromatics and covalently bound aromatics from Permian source rocks, their mass spectra are displayed in Fig. 7. Bflas (benzofluoranthenes), BePy (benzo(e) pyrene), BaPy (benzo(a) pyrene) and Perylene in this study were identified by comparison of mass spectra and by matching retention times with references reported previously [50,51]. In the free aromatics, only Bflas, BePy and BaPy were detected, and BePy obviously existed in all samples. Free perylene were not detected in all the Permian source rocks. The BePy were also identified in all the hydropyrolysates, but perylene were only identified in the Dalong Formation (GY-3, GY-8, WC-4A and WC-5).

BePy is considered to be sourced from planktonic algae [19], thus it exists in all the free and covalently aromatics. Perylene is a polycyclic aromatic hydrocarbon consisted of five rings, and extensively occurs in recent sediments and low mature source rocks [15,50,52–59]. Due to the thermodynamic instability [18,55,60–62] or easy degradation by way of weathering [63], free perylene has only been identified in low mature geologic samples and oils. All the investigated samples are mature or over mature samples selected from outcrops, with the inevitable influence of thermal alteration and water washing. Thus, perylene is absent in all the free aromatics. However, perylene was detected in the hydropyrolysates of the Dalong Formation kerogen. It implied the covalently bound perylene was protected by macromolecular structure from the destruction by thermal stress and weathering.

Perylene in geologic samples is widely considered to be terrestrial origin [15,50,55,63–66]. Therefore, the absence of covalently bound perylene in the Wujiaping Formation (NJ-3) and the Changxing Formation (WCLD-1) were probably due to their marine origin [31], while the existence of covalently bound perylene in the Dalong Formation in the Guangyuan and the Wangcang areas might indicate their possible terrestrial high-plants input. Previous studies have confirmed this speculation. The visual kerogen analysis by Wu

et al. [67] reported the presence of massive vitrinite in the Dalong Formation in Guangyuan areas. Meanwhile, Wang et al. [28] and Li et al. [30] also found the characteristics of gravity current deposition, such as microscopic graded layer and disorderly arranged biodetritus, in the Dalong Formation in the Sichuan Basin. However, since the Wujiaping Formation and the Changxing Formation have higher maturity level than the Dalong Formation samples (Fig. 6), thermal alteration might be another reason for the absence of covalently bound perylene in the samples of NJ-3 and WCLD-1.

Whereas, not all the samples with terrestrial high-plants input can find the existence of perylene. The Longtan Formation in the Sichuan Basin are dominantly terrestrially derived [68], but without the presence of covalently bound perylene. Meanwhile, the maturity of LF-2 (Ro: 1.6%) is lower than that of WC-5 (Ro: 1.8%). It means the absence of covalently bound perylene in LF-2 is not attributed to thermal alteration. Recently, more and more works confirm that the perylene is a product generated by wood-decaying organisms under anaerobic environments [15,18,57,66]. Thus, the generation of perylene in geological samples depends on the terrestrial input and the anaerobic condition. Oxidizing depositional environments were not suitable for the prosperity of perylene-forming microbes. In Sichuan Basin, the depositional environment for most of the Dalong Formations were reducing [30], but were oxidizing for the Longtan Formation [68]. Therefore, covalently bound perylene was identified in the Dalong Formations but absent in the Longtan Formations. It implied that the existence of covalently bound perylene might indicate terrestrial high-plant inputs in the anaerobic environment.

3.2. Artificial simulation sequence

In order to confirm the above discussions further, a mature source rock from Dalong Formation (GY-8) was selected for anhydrous pyrolysis simulation experiments. The distributions of aromatic hydrocarbons of both artificial simulation products and hydropyrolysates released from thermally altered kerogen at various maturities were discussed and compared with the above natural maturity sequence.
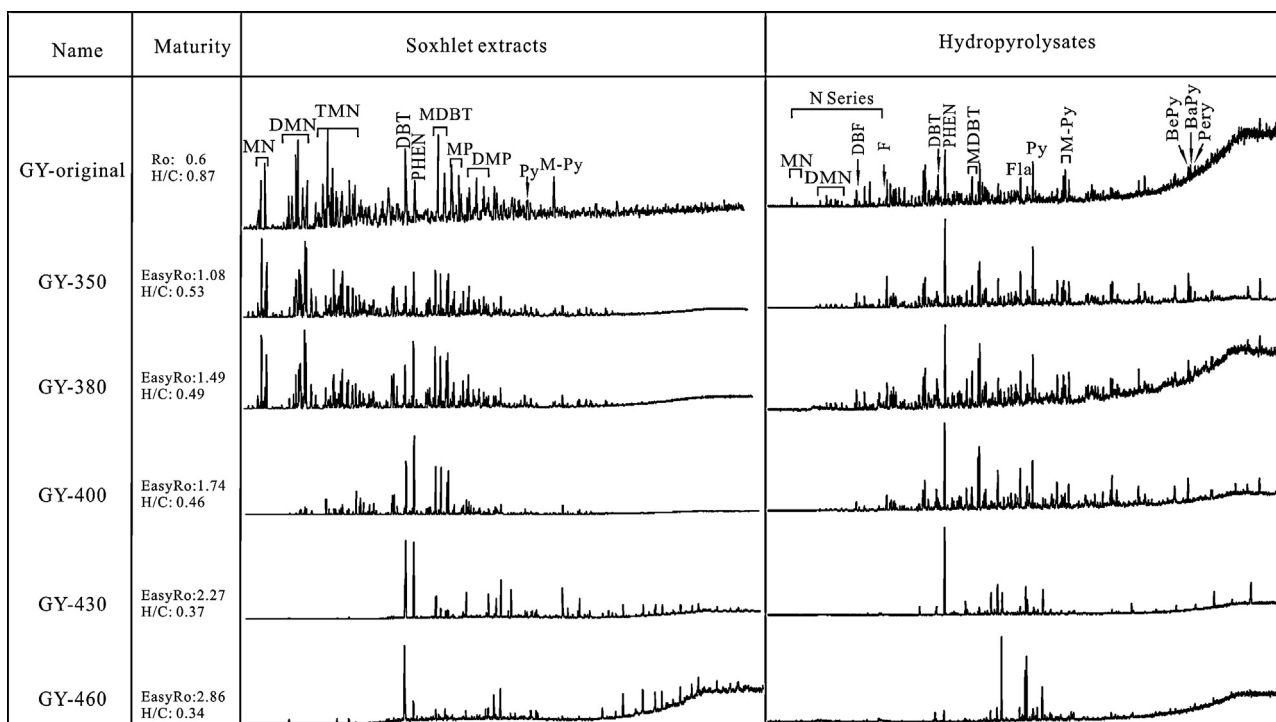
Fig. 8. TIC chromatograms of aromatic hydrocarbons in soxhlet extracts (free state) and hydropyrolysates (covalently bound state) in artificial simulation sequence and its original sample.

The distributions of aromatic compounds in the extracts of original sample and its thermal maturation products have systematic changes with simulation temperature (Fig. 8). The naphthalenes, phenanthrenes and benzothiophene compounds are abundant in the extracts of original sample, thermal altered kerogen at 350 °C and 380 °C. As temperatures continue to increase, the relative concentration of naphthalenes decreased at 400 °C and disappeared at 430 °C and 460 °C. This phenomenon is consistent with that in natural sequence. It implied that naphthalenes are possibly easier thermal altered than other aromatic compounds. For the hydropyrolysates, the distribution of aromatic compound of original sample is quite similar to those of thermal altered kerogens at the simulation temperature of 350 °C, 380 °C and 400 °C, but it is different to those at the temperature of 430 °C and 460 °C (Fig. 8). It seems that the aromatic hydropyrolysates at 430 °C and 460 °C were severely
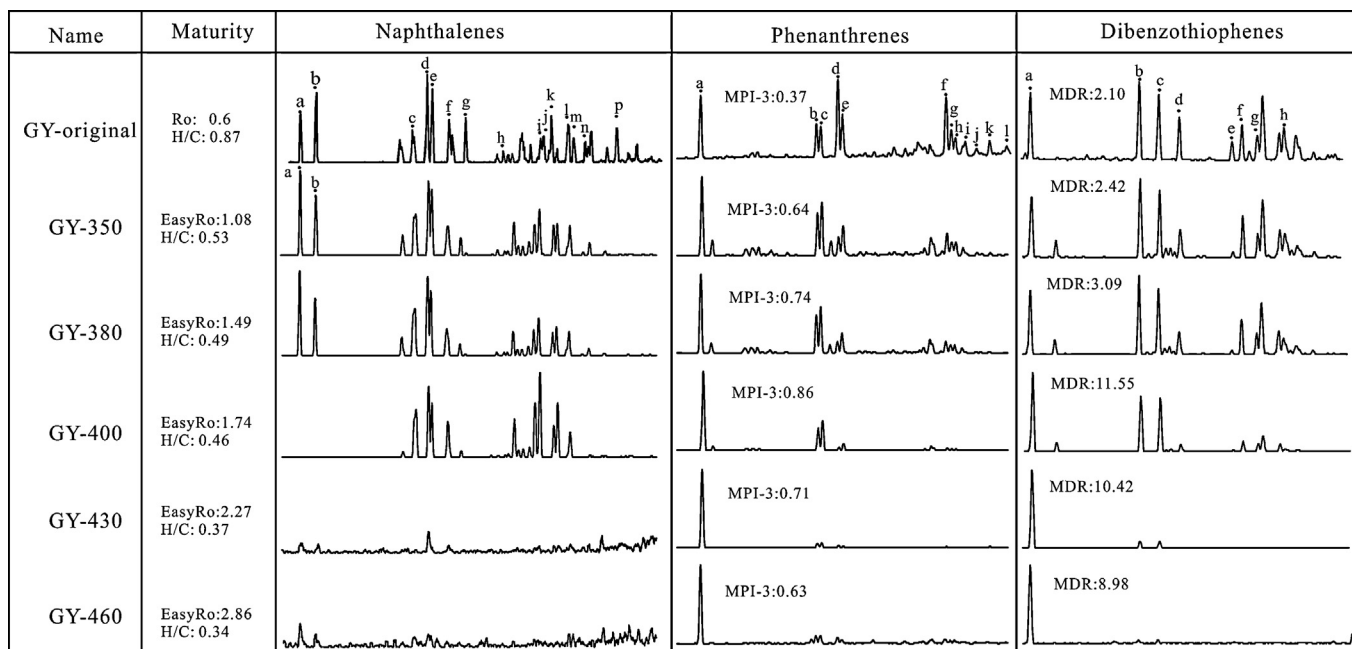

Fig. 9. Representative partial expanded gas chromatograms–mass spectrometry of the free aromatic fractions in artificial simulation sequence and its original sample with peak identifications in Table 3.
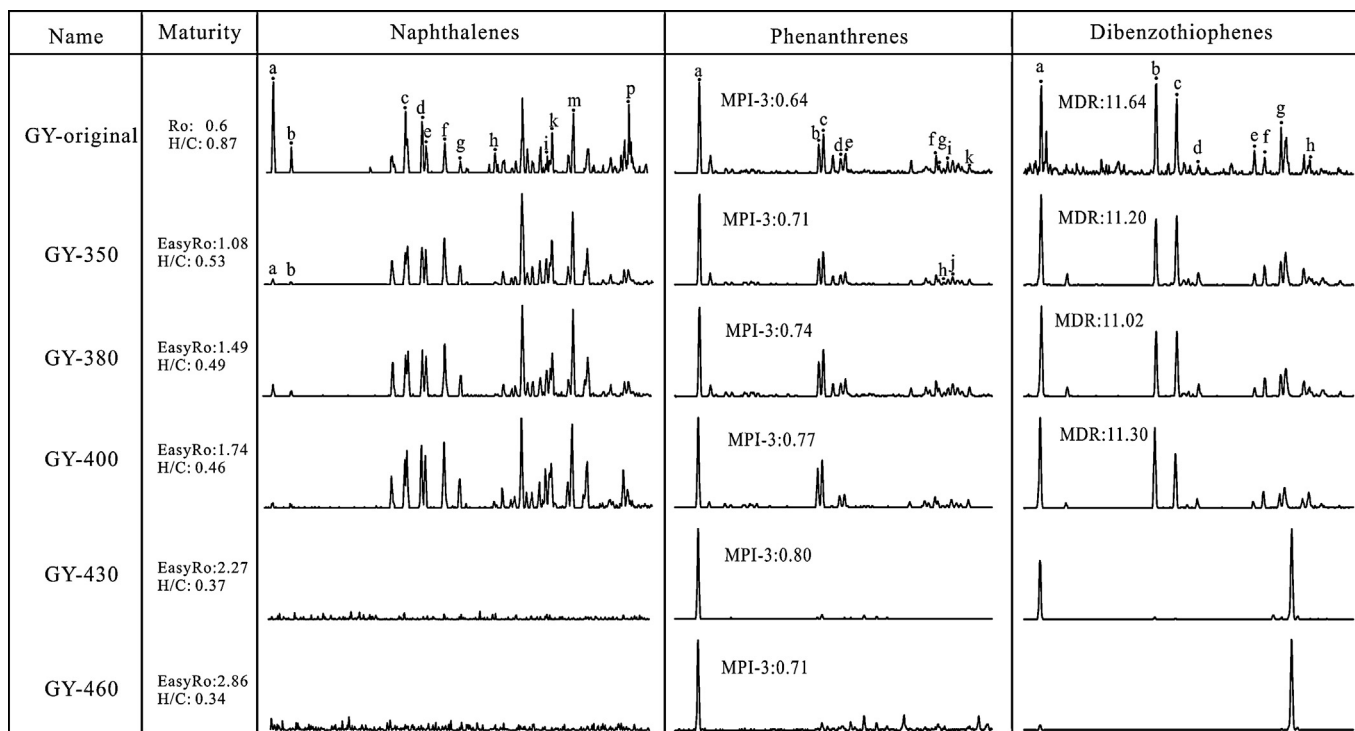
Fig. 10. Representative partial expanded gas chromatograms–mass spectrometry of the covalently bound aromatic fractions in artificial simulation sequence and its original sample with peak identifications in Table 3.
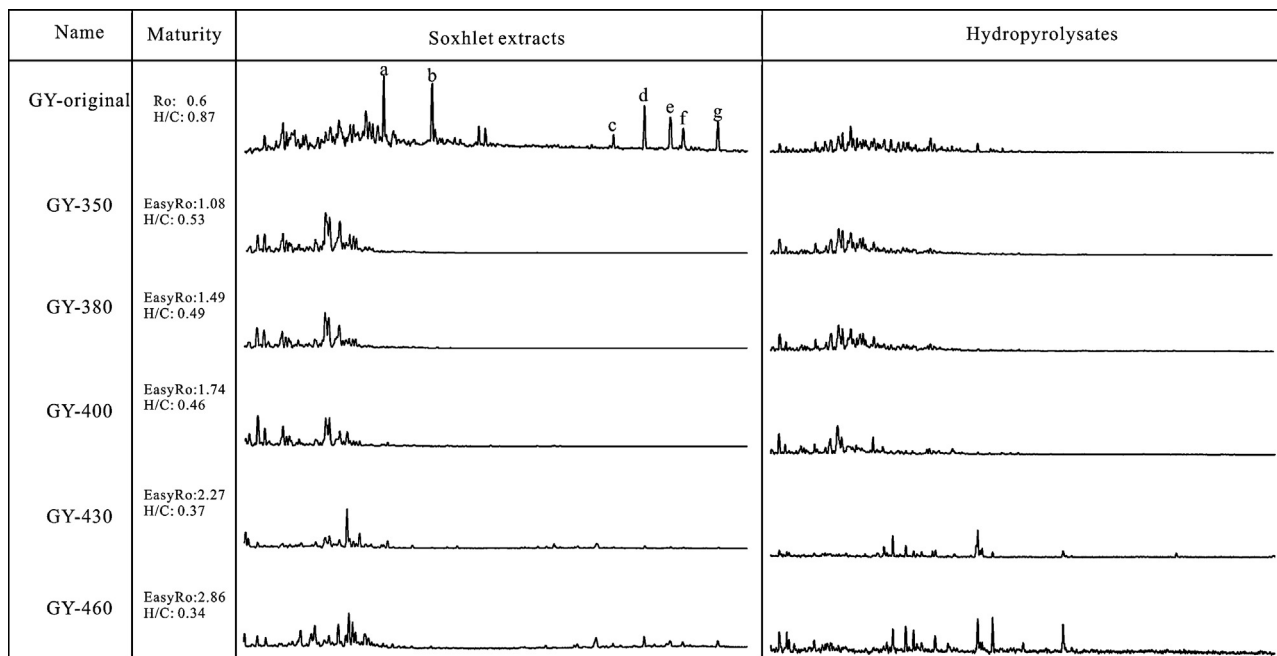

Fig. 11. Triaromatic (*m/z* 231) distribution of aromatic hydrocarbons obtained by Soxhlet extraction and by HyPy in artificial simulation sequence and its original sample. Labeled peaks are identified in Table 4.

thermally altered, which means aromatic compounds within kerogen will finally be altered by high thermal stress.

3.2.1. Naphthalenes, phenanthrenes and dibenzothiophenes

The α-substitution pattern substituted isomers (9-MP, 1-MP and 1-MDBT) are predominant compounds in the Soxhlet extract of the original sample (GY-8). With the increasing simulation tem-

perature, the relative abundance of those α-substitution pattern substituted isomers gradually decreased (Fig. 9). The MPI-3 ratio and the MDR ratio is 0.37 and 2.10, respectively, in the original sample, and then gradually increased into 0.86 and 11.55, respectively, at 400 °C (Table 2). They are both increased with simulation temperature. However, covalently bound aromatics for all investigated samples display a very similar distribution of methylphenan-
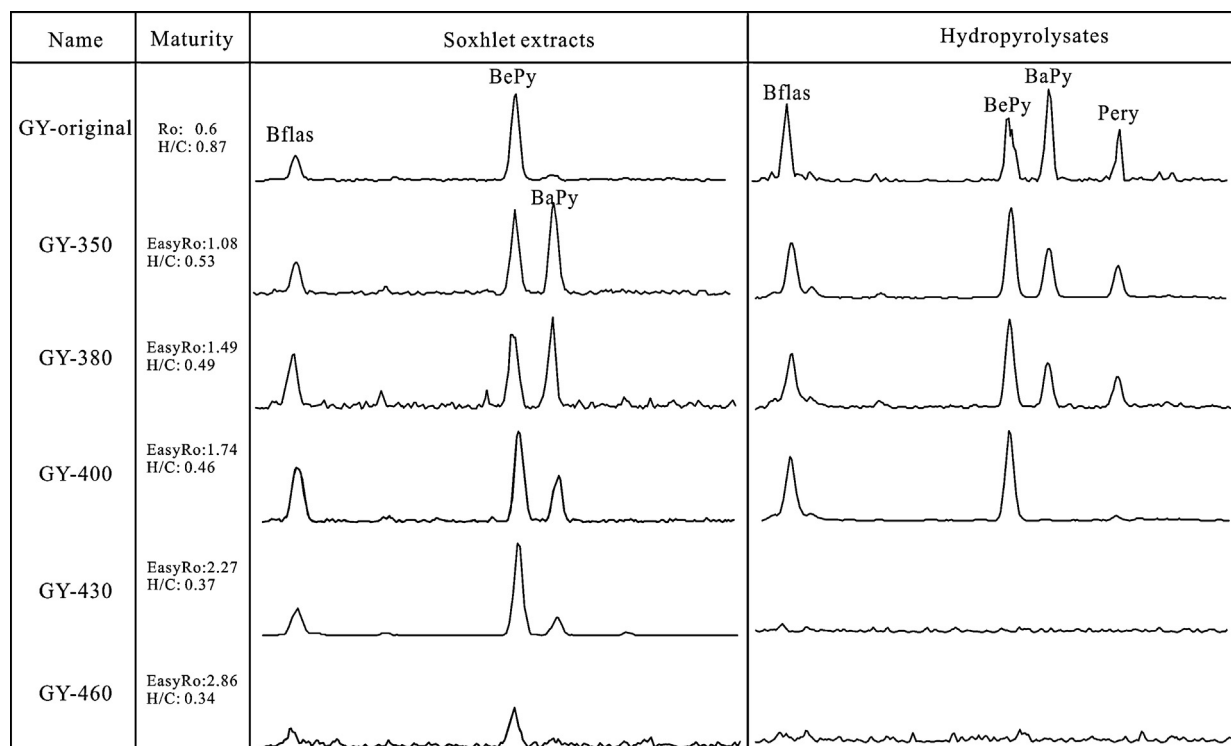
Fig. 12. The *m/z* 252 gas chromatograms–mass spectrometry of aromatic hydrocarbons obtained by soxhlet extraction and by HyPy in artificial simulation sequence and its original sample.

threnes and methyldibenzothiophenes (Fig. 10). The MPI-3 ratio and MDR ratio is 0.64 and 11.64 in the hydropyrolysate of the original sample, respectively. The MPI-3 ratio slightly increased with simulation temperature and reached the highest value of 0.80 at 430 °C, while the MDR ratio is quite stable (about 11.0) for all temperatures. The MPI-3 ratio for the hydropyrolysate of thermal altered kerogen at 400 °C (Easy Ro: 1.74%) is 0.77, which is similar to that for WC-5 (Ro: 1.8%). Thus, the results from the artificial simulation sequence and the natural maturity sequence are comparable.

As we discussed above, the distributions of methylphenanthrenes in the hydropyrolysates cannot be explained as the results of maturation, but probably were the original distribution characteristics within kerogen. Meanwhile, the increment of MPI-3 ratio with temperature for the hydropyrolysate is quite slower than that for the thermal simulation product. It was further confirmed that the rearrangement of methyl group on the aromatic nucleus should be suppressed due to the protection of kerogen macromolecular structure.

3.2.2. Aromatic steroids

The triaromatic steroids were not detected in both the kerogen thermal maturation products and their corresponding hydropyrolysates (Fig. 11). The absence of triaromatic steroids in the hydropyrolysates from thermal altered kerogens of all temperatures is consistent the results of natural maturity samples of the Dalong Formation. Beach et al. [69] pointed out that triaromatic steroid hydrocarbons can be thermal altered at laboratory experiments of 200 °C. Therefore, the absence of triaromatic steroids in the kerogen thermal maturation products is probably the results of very high experiment temperature. Though aromatic steroid hydrocarbons have been detected in source rock heating experiments by Mackenzie et al. [49], their experiment temperature (200–285 °C) is lower than pyrolysis temperature used here (350–460 °C). Meanwhile, the influence of HyPy technique on it

released biomarkers is very small because of the use of high pressure hydrogen and the short residence time of hydropyrolysate in the hot pyrolysis tube [21,22]. Thus, the absence of triaromatic steroids in the hydropyrolysates from thermal altered kerogens of all temperatures should not be due to the high temperature that HyPy technique used, while possibly because the aromatization of covalently bound steroids were prohibited to some extent by the protection of macromolecular structure.

Furthermore, since the hydropyrolysates at 430 °C and 460 °C were severely thermally altered (Fig. 8), aromatization and condensation probably occur extensively within the thermal altered kerogens at 430 °C and 460 °C. However, the triaromatic steroids were still absent in the hydropyrolysates of those thermal altered kerogens. It also confirms our speculation that the side chain of covalently bound steroid will be cracked before the aromatization within kerogen. Therefore, aromatic steranes cannot be detected in the hydropyrolysates from thermal altered kerogens at 430 °C and 460 °C, since the biogenic carbon skeletons of covalently bound sterenes were destroyed before aromatization reaction.

3.2.3. Perylene

Perylene was detected in the hydropyrolysate of original sample (GY-8). As we discussed above, the covalently bound perylene can be protected by macromolecular structure from the destruction by thermal stress and weathering. For the artificial simulation sequence, perylene is absent in all of kerogen thermal maturation products, but it is detected in the hydropyrolysates of thermal altered kerogens at 350 °C and 380 °C (Fig. 12). Covalently bound perylene was not found in thermally altered kerogen with the simulation temperature more than 400 °C. It implies that covalently bound perylene can occur at a H/C ratio of >0.49 (simulation temperature lower than 400 °C). This result is completely consistent with the above study on natural maturity samples of the Dalong Formation, which the covalently bound perylene can be detected on the hydropyrolysates of overmature Dalong Formation kerogens.

The Ro values of those overmature Dalong Formation kerogens are about 1.8%, and their H/C values are in the range of 0.53–0.55. Therefore, the covalently bound perylene can be protected by macromolecular structure from the destruction of thermal stress at least below Ro of 1.8% (or H/C > 0.5).

4. Conclusions

This study compared the characteristics of covalently bound aromatics with the free counterparts from various Permian source rocks with different maturities in the Sichuan Basin. Furthermore, one mature source rock from Dalong Formation (GY-8) was selected for anhydrous pyrolysis simulation experiments. The results from the artificial simulation experiments are quite consistent with those from natural maturity sequence. Based on the above discussion, the following conclusions can be made:

(1.) The protection of kerogen macromolecular structure suppresses rearrangement of methyl group on the aromatic nucleus and the aromatization of steroids probably prohibits to some extent before the maturity of Ro < 2.4%. In the covalently bound aromatics, the aromatic thermal maturity parameters based on the aromatization and rearrangement might be invalid.

(2.) The perylene precursor in the kerogen can be protected by macromolecular structures from thermal alteration (at least Ro < 1.8% or H/C > 0.5). The covalently bound perylene has the potential to be used as a marker for terrestrial high-plant inputs in the anaerobic environment.

Acknowledgements

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