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Characterization of alkyl phenanthrene distributions in Permian Gondwana coals and coaly shales from the Barapukuria Basin, NW Bangladesh

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Abstract

Coals and coaly shales from the Permian Gondwana sequence in the Barapukuria Basin (core GDH-40) of Bangladesh were investigated to determine the influence of rock type and organic source on methylphenanthrene (MP) maturity parameters such as methylphenanthrene ratio (MPR) and methylphenanthrene index 3 (MPI 3). The T_{\max} (°C) depth profile of the coals is almost constant, and the T_{\max} values (430–440°C) correspond to about 0.6–0.7% vitrinite reflectance, which suggests the early stage of oil generation. In the constant maturation stage, the MPR and MPI 3 values of coals are clearly different from those of coaly shales. The 9-MP/1-MP and 9-MP/2-MP ratios of the coals are higher than those of the coaly shales because the activated methylation preferentially leads to 9-MP in coals during the early stage of oil generation. Also, these ratios increase in the coals rather than coaly shales attributed to selective biodegradation of the MP and conifer-rich sources. A negative correlation observed between 9-MP and 2-MP compositions indicates methylation effect and/or change in organic source input into the paleomire. The 1,7-dimethylphenanthrene (DMP) isomer, gymnosperm-derived pimanthrene, is more abundant in the coals than the coaly shales. The relative abundances of the 1,7-DMP in the coals tend to be higher in middle part of the drill core, and decrease with depths. Anthracene (A) and methylanthracene (MA) also tend to be more abundant in the coals. The abundance of 1,7-DMP, A and MA in the coals may be related to Gondwana coals characterized by the predominance of coniferous gymnosperms.

1. Introduction

Tricyclic aromatic hydrocarbons such as phenanthrene (P) and methylphenanthrenes (MP) are used as parameters of thermal maturity for carbonaceous shales containing type III kerogen. Organic source and types sometimes affect the MP maturity parameter in the early stage of oil generation (e.g. Radke et al.,

1982a, 1982b, Radke, 1987; Garrigues et al., 1988; Sampei et al., 1994; Alexander et al., 1995; Kaneko and Takeda, 1995; Hossain et al., 2009; Szczerba and Rospondek, 2010). However, the influence and sensitivity of organic source on this parameter between coaly shale and coal layers has not been quantified. Thus, we investigated coals and coaly shales from the Permian Gondwana sequence, Bangladesh to evaluate

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the influence of organic source on the MP maturity parameters. The Permian Gondwana sequence in the Barapukuria Basin of NW Bangladesh contains abundant coal seams and coaly shales (e.g. Khan, 1991; Bakr et al., 1996; Islam and Hossain, 2006; Islam and Hayashi, 2008; Hossain et al., 2013), but to date organic geochemical studies have been limited, especially for triaromatic hydrocarbons.

2. Geologic setting of Barapukuria Basin

The Bengal Basin is located in the northeastern part of Indian subcontinent, between the Indian Shield to the west and the Indo-Burman Ranges to the east, north is Shillong Massif and it plunges into the Bay of Bengal towards south (Fig. 1). The northwestern Bengal Basin of Bangladesh was initially connected with Indian landmass, South Africa, Antarctica and Australia making a wide continental supper group named Gondwanaland (Reimann, 1993; Imam, 2013). The initiation of Bengal Basin began during Late Jurassic to Early Cretaceous with the rifting of the Indian continent from Antarctica-Australia (Banerji, 1981;

Reimann, 1993; Alam et al., 2003). During Early to Late Cretaceous, the breakup of Gondwana, the Indian continent rapidly drifted towards north (Reimann, 1993; Frielingsdorf et al., 2008). Tectonically, this basin has been evolved by the continental collision between Indian plate and Eurasian plate, building the widespread Himalayan Mountain belt in the north and Indo-Burman Ranges in the east (Fig. 1). Bangladesh occupies a major part of the Bengal Basin, northwestern part of it is filled by very thick (>825 m) Permian Gondwana sediments (Hossain et al., 2002). The coal bearing Barapukuria Basin, covering an area of approximately 6.75 km² (Islam et al., 2003), is located in the Rangpur platform of the stable shelf zone in the NW Bangladesh (Fig. 1). This area lies between the latitudes 25°31'45" to 25°33'50" N and the longitudes 88°57'48" to 88°58'53" E. The studied drill hole GDH-40, is the deepest well among the others well investigated, located in the central eastern part of the Barapukuria Basin. The stratigraphy of the Gondwana succession in the Barapukuria Basin is given in Table I and Fig. 2.

Precambrian Basement Complex is underlying the Permian Gondwana Group consists predominantly of diorite, granodiorite, quartzdiorite and granite (Khan, 1991; Bakr et al., 1996; Islam and Hayashi, 2008). The upper contact of the Precambrian Basement Complex is erosional. The Gondwana sequence in the Barapukuria Basin comprised almost entirely of arkosic sandstone and coal, unconformably overlain by 136 m of water-bearing, unconsolidated Tertiary to Recent sediments (Norman, 1992). Maximum thickness of the Gondwana Group is 476 m encountered in the drill hole GDH-40 (Fig. 2). The unconformably overlying Gondwana Group is Dupitila Group of the Pliocene age. The lower Dupitila Formation mainly consists of sandstone, mudstone and white clay, and the upper Dupitila Formation consists chiefly of sandstone, pebbly sandstone, and clay/mudstone. The Pleistocene Barind Clay Formation is underlain by the upper Dupitila Formation and comprises yellowish to reddish brown clay and silty clay (Bakr et al., 1996; Islam and Hossain, 2006). The uppermost part of the succession is Holocene alluvium, consists mainly sand, silt and clay.

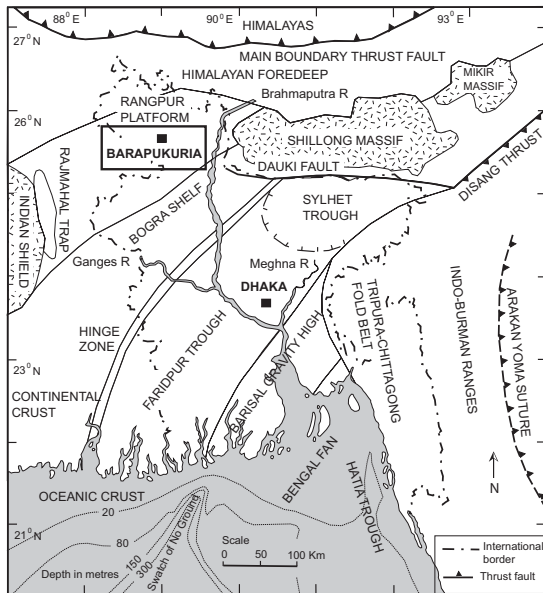


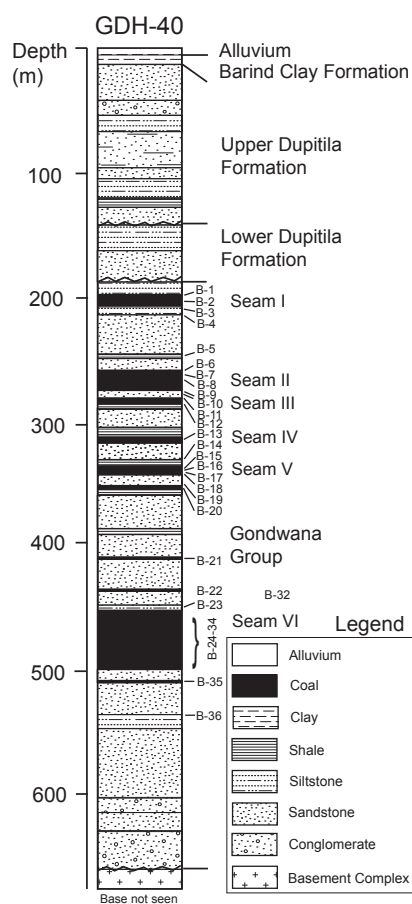
Fig. 1. Generalized map showing location of the study area and main geographic features of the Bengal Basin and adjoining areas (modified after Alam et al., 1990; Khan, 1991; Reimann, 1993).

Table 1. Stratigraphy of the Barapukuria Basin, NW Bangladesh (modified after Bakr et al., 1996).

Age	Rock sequences	Lithological description	Maximum thickness (m)
Holocene	Alluvium	Sand, silt, clay	2
Pleistocene	Barind Clay Formation	Clay and silty clay	10
Pliocene	Upper Dupitila Formation	Sandstone, pebbly sandstone and clay/ mudstone	127
	Lower Dupitila Formation	Sandstone, mudstone and white clay	
Permian	Gondwana Group	Feldspathic sandstone, carbonaceous sandstone, siltstone, shale, coal and conglomerate/tillite	476
Precambrian	Basement Complex	Diorite, granodiorite, quartzdiorite, granite, schist and gneiss	14+

3. Materials and Methods

Thirty-six samples (23 coals and 13 coaly shales) were collected from drill hole GDH-40 in the depth range 195–535 m below surface (Fig. 2). All coal and coaly shale samples were pulverized in an iron mortar and pestle. Total organic carbon (TOC) content was determined using a CHNS elemental analyzer (FISSION, EA 1108). T_{max} values were obtained using a Rock-Eval instrument. Approximately 20 g powdered samples were extracted using Soxhlet apparatus with a mixture (9:1) of DCM (dichloromethane) and MeOH (methanol) for 72 h. The extracts were then separated into aliphatic and aromatic fractions, using activated TLC (Kieselgel 60 PF254, Merck). Gas chromatography–mass spectrometry (GC–MS) was conducted on 36 extracted aromatic hydrocarbon fractions using a Shimadzu QP2010 with a fused silica column (DB-5MS; 30 m × 0.25 mm i.d.). The GC oven temperature was programmed from 50°C to 300°C, at a rate of 8°C/min. Helium was used as the carrier gas. The MS had an ionization potential of 70 eV, scan range of m/z 50 to 850, and scan rate of 0.5 s. P (m/z 178), A (anthracene, m/z 178), MP (m/z 192), MA (methylanthracene, m/z 192) and DMP (dimethylphenanthrene, m/z 206) compounds were identified by comparison of retention times and mass spectra with published data and standard PAH Solution Mix (Accu Standard Inc., Z-013-17).


Fig. 2. Summarized lithostratigraphic column of the drill hole GDH-40 showing sampling points of the Barapukuria Basin, NW Bangladesh (modified after Bakr et al., 1996; Islam et al., 2004; Islam and Hossain, 2006).

4. Results and discussion

Relative proportions (area% of mass chromatograms) of triaromatic hydrocarbons and their isomer ratio values in the coals and coaly shales are shown in Table 2 and 3.

4.1. Thermal maturity

Alkyl phenanthrene distributions are widely used as maturity parameters based on their thermal stability of individual isomers (e.g. Radke et al., 1982a, 1982b; Angelin et al., 1983; Radke, 1987). Among the MP isomer compounds, α -substitution (1-MP and 9-MP) show less thermodynamic stability over related isomers with β -substitution (2-MP and 3-MP) (Fig. 3 : Radke et al., 1982a, 1982b; Radke and Welte, 1983; Radke et al., 1986; Radke, 1987; Szczerba and Rospondek, 2010). The predominance of 2-MP and 3-MP over 1-MP and 9-MP is utilized in maturity parameters such as methylphenanthrene ratio (MPR, [2-MP/1-MP]) and methylphenanthrene index 3 (MPI 3, [2-MP+3-MP]/[1-MP+9-MP]) (Radke et al., 1982a; Angelin et al., 1983; Radke et al., 1986; Radke, 1987; Appendix A). Figure 4 shows the depth profiles of the bulk maturity parameter T_{\max} , MPR, and MPI 3. T_{\max} ($^{\circ}\text{C}$) of the coals is constant from 200 m to 450 m, but increases slightly with increasing depth from 450 m to 550 m (Table 2). T_{\max} values of 430 to 440 $^{\circ}\text{C}$ in Table 2 correspond to vitrinite reflectance (R_o) of ~ 0.6 -0.7% (Tissot and Welte, 1984), suggesting the early stage of oil generation. MPR and MPI 3 of the coals (Fig. 4) are also almost constant, with a slight increase in the lower part (450 m to 550 m). However, MPR and MPI 3 values of the coaly shales are clearly higher than those of coals at 200 m to 450 m depth, implying a difference in the other factors as discussed below between coaly shales and coals. Average MPI 3 values of coal and coaly shale are 0.69 ± 0.09 ($n=23$) and 0.80 ± 0.17 ($n=13$), respectively, and average MPR values are 1.15 ± 0.16 ($n=23$) and 1.28 ± 0.28 ($n=13$), respectively. Thus, MPR and MPI 3 values of the coaly shales are about 0.1 greater than those of the coals.

4.2. Effect of methylation

Radke et al. (1982a) reported that methylation processes of P may take place during diagenesis, and 9-MP is readily produced at the beginning of the methylation processes among the PM isomers. Therefore, predominance of 9-MP in the immature and slightly matured sediment samples possibly associated with alkylation processes (Budzinski et al., 1997). The 9-MP/1-MP and 9-MP/2-MP ratios of the coals are both greater than the ratios in the coaly shales from the same layers (Figs. 5a, b). This could be due to an activated methylation to 9-position of P in the coals during the early stage of oil generation, because coals have many methyl moieties more than coaly shales. A methyl transfer to P from a terpenoid alcohol with a gem-dimethyl and/or polymethyl aryl carotenoid moiety abundant in coals can preferentially lead to 9-MP due to a relatively lower energy barrier (Szczerba and Rospondek, 2010). Among five MP isomers (1-MP, 2-MP, 3-MP, 4-MP and 9-MP), the energy barrier of 9-MP from P is the lowest, and that of 2-MP is the highest (Szczerba and Rospondek, 2010). Consequently, the difference of the 9-MP/2-MP values between the coals and coaly shales could be larger than that shown by 9-MP/1-MP in Figs. 5a, b. A clear negative correlation exists between 9-MP and 2-MP (Fig. 6; $2\text{-MP} = -0.354 \times 9\text{-MP} + 36.6$, $r = -0.53$). These suggest that concentration of such terrestrial organic matters with abundant methyl as terpenoid alcohol having gem-dimethyls and polymethyl aryl carotenoid could control the values of MPR and MPI 3 in the early stage of diagenesis. This effect could be more highly activated in very high TOC sediments like coal rather than coaly shale.

4.3 Effect of biodegradation

Distributions of alkyl phenanthrene isomers in coal and sediment are also depend on extent of biodegradation in the subsurface environments (Rowland et al., 1986; Peters and Moldowan, 1993). Biodegradations are common in the peat bogs (Couch, 1987; Ahmed et al., 1999). Alkyl phenanthrenes are less susceptible than P during microbial degradation (Resistant strength: DMP

Table 2. Concentrations of investigated triaromatic hydrocarbons (as the percentage of separate identified *m/z* mass chromatograms) in Permian Gondwana coals and coaly shales from the Barapukuria Basin, NW Bangladesh.

Sample no	Lithology	Coal seam	Depth (m)	Phenanthrene and anthracene (<i>m/z</i> =178)	Methylphenanthrene and methylanthracene (<i>m/z</i> =192)										Ethylphenanthrene and dimethylphenanthrene (<i>m/z</i> =206)						TOC (%)	<i>T</i> _{max} (°C)		
					P	A	3-MP	2-MP	MA	9-MP	1-MP	3-EP	2-EP	9+1-EP +3,6-DMP	3,5+2,6-DMP	2,7-DMP	1,3+2,10 +3,9+3,10-DMP	1,6+2,9	1,7-DMP	2,3+1,9 +4,9+4,10-DMP			1,8-DMP	1,2-DMP
B-1	Coal	Seam I	195.38	93.2	6.8	15.2	24.4	24.4	3.1	36.6	20.6	4.5	5.9	6.8	6.2	6.0	23.8	9.8	12.7	12.1	7.1	5.2	53.8	435
B-2	Coal	Seam I	197.51	33.3	66.7	11.0	23.7	3.4	38.4	23.5	2.5	3.1	4.9	7.1	7.1	7.1	22.9	13.4	14.9	13.9	4.3	5.4	48.3	437
B-3	Coaly shale		199.03	95.7	4.3	18.0	27.1	0.3	36.8	17.8	3.7	4.1	5.8	7.1	5.5	29.0	15.2	10.2	11.6	3.8	4.1	3.3	460	
B-4	Coaly shale		213.36	97.6	2.4	15.7	23.7	0.2	41.2	19.3	3.1	3.6	5.8	9.0	5.9	26.7	12.5	11.5	12.9	3.8	5.2	2.3	483	
B-5	Coaly shale		254.20	20.3	79.7	5.9	17.2	4.5	48.8	23.6	1.6	3.4	5.6	6.0	6.0	23.3	13.4	13.6	12.8	6.7	7.7	12.3	478	
B-6	Coal	Seam II	254.51	92.2	7.8	13.6	24.1	1.5	41.2	19.5	4.0	4.1	7.1	6.3	5.7	23.6	12.2	13.2	13.0	5.3	5.6	74.2	432	
B-7	Coal	Seam II	257.56	94.7	5.3	15.4	24.3	1.0	38.7	20.6	3.6	3.8	6.8	7.2	5.9	21.4	11.7	14.0	14.0	6.1	5.6	57.5	432	
B-8	Coaly shale		259.69	97.3	2.7	16.7	28.0	0.2	34.8	20.3	3.4	3.3	7.5	7.8	6.6	23.3	10.2	13.5	12.4	6.3	5.7	16.8	445	
B-9	Coal	Seam II	266.70	90.6	9.4	14.5	22.4	1.2	44.5	17.4	5.1	4.9	7.1	7.3	8.4	23.4	11.6	10.5	11.4	5.4	5.0	68.6	435	
B-10	Coaly shale		268.22	96.9	3.1	15.4	25.9	5.4	34.0	19.3	4.9	3.9	6.8	6.7	5.1	24.1	7.6	18.1	12.7	6.0	4.3	n.a.	n.a.	
B-11	Coaly shale		276.45	98.7	1.3	19.8	28.5	0.2	33.4	18.2	6.0	4.4	8.6	8.0	6.2	25.0	12.2	10.8	10.4	4.5	4.2	7.0	445	
B-12	Coal	Seam III	282.24	89.6	10.4	14.6	23.2	0.7	42.0	19.6	3.2	3.0	4.7	7.0	7.2	21.6	14.0	15.8	12.8	5.7	4.8	59.6	431	
B-13	Coal	Seam IV	306.93	91.7	8.3	16.2	25.2	2.0	37.2	19.5	4.0	4.3	5.3	7.8	8.1	21.3	13.1	15.4	11.9	4.7	4.0	40.3	433	
B-14	Coaly shale		308.46	98.1	1.9	18.3	27.9	0.2	33.4	20.2	5.5	5.5	7.5	7.6	6.3	22.0	11.7	12.3	10.2	6.5	5.0	15.5	432	
B-15	Coal	Seam V	331.01	96.3	3.7	15.8	22.3	0.5	39.8	21.6	4.4	4.4	6.4	7.0	6.0	21.5	12.2	15.6	10.8	6.1	5.6	69.9	434	
B-16	Coaly shale		332.23	97.3	2.7	18.9	25.0	0.9	31.2	24.2	7.7	5.6	9.7	6.2	3.8	21.2	3.6	9.2	10.2	15.7	7.3	30.3	430	
B-17	Coal	Seam V	332.54	99.2	0.8	17.0	19.5	0.4	42.0	21.1	4.8	4.9	6.2	6.4	3.6	26.1	11.3	14.4	10.9	5.9	5.5	34.9	437	
B-18	Coal	Seam V	335.58	91.4	8.6	16.2	19.0	9.5	37.9	17.5	5.8	5.4	6.2	6.8	6.8	25.5	9.0	13.8	10.9	5.7	4.2	59.1	435	
B-19	Coaly shale		336.19	98.2	1.8	20.1	28.6	0.9	29.5	20.9	5.1	3.6	6.5	8.5	7.3	20.7	11.7	16.1	10.5	5.4	4.7	4.6	448	
B-20	Coal		345.34	96.4	3.6	17.3	26.0	0.8	31.7	24.2	3.7	3.2	5.1	6.0	6.8	19.9	10.9	21.8	11.5	6.3	4.8	70.6	432	
B-21	Coal		407.52	91.9	8.1	16.5	20.8	2.1	39.6	21.0	3.6	3.8	5.6	5.2	6.1	20.8	10.2	20.5	12.9	6.6	4.9	55.7	430	
B-22	Coal		438.91	93.3	6.7	18.7	22.9	3.4	39.6	15.4	4.3	3.8	7.0	7.6	7.2	23.6	7.8	18.2	10.8	5.1	4.7	74.4	432	
B-23	Coaly shale		449.88	98.9	1.1	17.5	25.0	0.1	34.0	23.6	5.2	3.9	7.6	7.4	6.2	22.8	8.0	13.3	10.7	9.5	5.5	9.3	432	
B-24	Coal	Seam VI	454.15	96.3	3.7	17.6	26.6	1.6	30.7	23.5	5.4	3.8	7.0	6.9	5.8	20.2	7.4	16.9	10.1	10.7	5.9	62.4	432	
B-25	Coal	Seam VI	457.20	94.5	5.5	14.4	25.2	7.6	34.0	18.9	4.0	3.4	5.8	7.8	5.8	26.2	8.4	16.3	12.6	5.3	4.5	56.3	434	
B-26	Coal	Seam VI	463.30	88.1	11.9	18.0	16.8	11.5	35.4	18.3	3.7	4.0	6.4	7.2	5.5	26.3	8.4	18.2	10.2	5.1	5.1	75.7	432	
B-27	Coal	Seam VI	471.83	87.4	12.6	18.3	19.6	11.2	30.8	20.2	3.7	3.2	4.2	6.0	7.0	5.0	26.4	7.1	20.3	10.6	6.0	5.1	72.5	434
B-28	Coal	Seam VI	475.49	88.9	11.1	17.9	19.7	6.7	35.0	20.8	2.2	2.8	5.5	8.4	7.2	26.6	6.3	15.6	11.5	6.7	7.2	60.2	436	
B-29	Coal	Seam VI	484.63	98.8	9.2	20.3	20.5	10.2	31.9	17.2	3.1	4.0	7.2	8.7	5.2	31.7	8.0	11.1	11.8	4.5	4.7	49.8	435	
B-30	Coal	Seam VI	489.51	88.0	12.0	16.6	21.4	9.7	33.6	18.7	3.6	4.9	7.0	8.3	6.8	29.7	9.8	10.1	11.7	3.9	4.1	64.3	436	
B-31	Coal	Seam VI	490.73	95.4	4.6	19.4	27.7	2.5	28.3	22.1	4.4	3.5	8.4	7.9	7.3	25.3	10.5	10.6	12.2	5.6	4.2	55.3	435	
B-32	Coaly shale		491.34	98.1	1.9	18.7	27.4	0.5	30.0	23.3	3.8	3.4	7.0	8.5	6.7	26.4	12.6	12.6	10.1	11.8	4.7	4.9	20.4	451
B-33	Coal	Seam VI	493.78	90.9	9.1	17.5	20.6	2.3	40.8	18.8	2.0	2.8	5.5	8.4	7.3	26.3	12.3	11.4	13.3	4.1	6.7	45.6	434	
B-34	Coaly shale		494.39	97.1	2.9	19.5	26.8	0.4	27.1	26.2	4.8	4.3	7.8	7.3	6.8	21.6	9.0	12.6	12.9	6.8	6.1	11.5	432	
B-35	Coal		505.97	96.9	3.1	19.6	22.4	0.6	42.3	15.0	2.9	4.8	6.7	8.0	5.7	30.5	11.8	9.5	11.9	3.5	4.7	32.5	436	
B-36	Coaly shale		535.23	99.3	0.7	22.2	27.4	0.1	35.3	15.0	1.9	3.9	7.0	10.9	6.3	33.3	11.4	6.3	12.9	2.8	3.4	4.0	498	

Abbreviations: P, phenanthrene; A, anthracene; MP, methylphenanthrenes; MA, methylanthracene; EP, ethylphenanthrenes; DMP, dimethylphenanthrenes; TOC, total organic carbon, n.a., not analyzed.

Table 3. Representative *m/z* 178, 192 and 206 mass chromatograms for phenanthrene (P), anthracene (A), methylphenanthrenes (MP), methylanthracene (MA), ethylphenanthrenes (EP) and dimethylphenanthrenes (DMP) of Permian coals and coaly shales, Barapukuria Basin, NW Bangladesh.

Sample no	Lithology	Coal seam	Depth (m)	A/(A+P)	MA/MP	P/MP	P/DMP	R_c (%)	MPI 3	MPR	DMPR	9-MP/3-MP	9-MP/2-MP	9-MP/1-MP	1,7-DMP/(1,3+2,10+3,9+3,10-DMP)
B-1	Coal	Seam I	195.38	0.07	0.031	0.96	1.04	0.64	0.69	1.18	0.36	2.40	1.50	1.78	0.53
B-2	Coal	Seam I	197.51	0.67	0.035	0.34	0.35	0.73	0.56	1.01	0.41	3.48	1.62	1.63	0.65
B-3	Coaly shale		199.03	0.04	0.003	0.96	1.04	0.62	0.82	1.52	0.29	2.05	1.36	2.07	0.35
B-4	Coaly shale		213.36	0.02	0.002	0.98	1.05	0.63	0.65	1.23	0.38	2.63	1.74	2.13	0.43
B-5	Coaly shale		254.20	0.80	0.047	0.21	0.21	0.62	0.32	0.73	0.33	8.25	2.84	2.07	0.59
B-6	Coal	Seam II	254.51	0.08	0.016	0.94	1.00	0.62	0.62	1.24	0.33	3.02	1.71	2.12	0.56
B-7	Coal	Seam II	257.56	0.05	0.010	0.96	1.02	0.65	0.67	1.18	0.40	2.51	1.59	1.88	0.66
B-8	Coaly shale		259.69	0.03	0.002	0.97	1.04	0.62	0.81	1.38	0.43	2.08	1.24	1.71	0.58
B-9	Coal	Seam II	266.70	0.09	0.012	0.92	1.01	0.60	0.60	1.28	0.45	3.07	1.99	2.55	0.45
B-10	Coaly shale		268.22	0.03	0.057	1.02	1.06	0.62	0.77	1.34	0.37	2.21	1.32	1.77	0.75
B-11	Coaly shale		276.45	0.01	0.002	0.99	1.10	0.66	0.94	1.56	0.38	1.69	1.17	1.83	0.43
B-12	Coal	Seam III	282.24	0.10	0.007	0.90	0.96	0.62	0.61	1.18	0.40	2.88	1.81	2.14	0.73
B-13	Coal	Seam IV	306.93	0.08	0.020	0.94	1.00	0.65	0.73	1.29	0.46	2.30	1.48	1.91	0.72
B-14	Coaly shale		308.46	0.02	0.002	0.98	1.10	0.66	0.86	1.38	0.42	1.83	1.20	1.65	0.56
B-15	Coal	Seam V	331.01	0.04	0.005	0.97	1.06	0.64	0.62	1.03	0.39	2.51	1.78	1.84	0.72
B-16	Coaly shale		332.23	0.03	0.009	0.98	1.12	0.62	0.79	1.03	0.41	1.65	1.25	1.29	0.43
B-17	Coal	Seam V	332.54	0.01	0.004	1.00	1.10	0.65	0.58	0.92	0.27	2.48	2.16	1.99	0.55
B-18	Coal	Seam V	335.58	0.09	0.104	1.01	1.03	0.63	0.64	1.09	0.39	2.34	1.99	2.16	0.54
B-19	Coaly shale		336.19	0.02	0.009	0.99	1.08	0.66	0.97	1.37	0.49	1.47	1.03	1.41	0.78
B-20	Coal		345.34	0.04	0.008	0.97	1.04	0.64	0.78	1.07	0.42	1.83	1.22	1.31	1.09
B-21	Coal		407.52	0.08	0.021	0.94	0.99	0.69	0.62	0.99	0.36	2.40	1.90	1.89	0.99
B-22	Coal		438.91	0.07	0.035	0.97	1.02	0.63	0.76	1.49	0.47	2.11	1.73	2.56	0.77
B-23	Coaly shale		449.88	0.01	0.001	0.99	1.09	0.65	0.74	1.06	0.44	1.95	1.36	1.44	0.59
B-24	Coal	Seam VI	454.15	0.04	0.016	0.98	1.06	0.67	0.82	1.14	0.46	1.74	1.15	1.31	0.84
B-25	Coal	Seam VI	457.20	0.05	0.082	1.02	1.02	0.62	0.75	1.33	0.39	2.36	1.35	1.80	0.62
B-26	Coal	Seam VI	463.30	0.12	0.130	1.00	0.95	0.62	0.65	0.92	0.37	1.97	2.11	1.93	0.69
B-27	Coal	Seam VI	471.83	0.13	0.126	0.98	0.94	0.66	0.74	0.97	0.35	1.68	1.57	1.52	0.77
B-28	Coal	Seam VI	475.49	0.11	0.071	0.95	0.94	0.65	0.67	0.95	0.47	1.96	1.78	1.69	0.59
B-29	Coal	Seam VI	484.63	0.09	0.114	1.01	0.98	0.69	0.83	1.19	0.35	1.57	1.56	1.86	0.35
B-30	Coal	Seam VI	489.51	0.12	0.108	0.97	0.96	0.67	0.73	1.14	0.38	2.03	1.57	1.79	0.34
B-31	Coal	Seam VI	490.73	0.05	0.025	0.98	1.04	0.66	0.93	1.25	0.42	1.46	1.02	1.28	0.42
B-32	Coaly shale		491.34	0.02	0.005	0.99	1.06	0.69	0.87	1.18	0.39	1.60	1.09	1.29	0.38
B-33	Coal	Seam VI	493.78	0.09	0.023	0.93	0.96	0.64	0.64	1.10	0.41	2.33	1.98	2.17	0.43
B-34	Coaly shale		494.39	0.03	0.004	0.98	1.07	0.67	0.87	1.02	0.46	1.39	1.01	1.03	0.58
B-35	Coal		505.97	0.03	0.006	0.97	1.05	0.68	0.73	1.49	0.32	2.15	1.89	2.81	0.31
B-36	Coaly shale		535.23	0.01	0.001	0.99	1.05	0.70	0.99	1.82	0.39	1.59	1.29	2.35	0.19

> MP > P; Ahmed et al., 1999), and especially 9-MP is highly resistant to biodegradation than 3-MP, 2-MP and 1-MP (Rowland et al., 1986). This effect may be the additional reason why the 9-MP/1-MP and 9-MP/2-MP ratios of the coaly shales are lower than those of coals in Figs. 5a and 5b. Aerobic biodegradation at oxic bottom of shallow water for peat deposition could be activated. Therefore, the effects of biodegradation are relatively more higher in the coal samples than in the coaly shales for the present study.

4.4. Effect of the origin of organic matter

The relative distribution of alkyl phenanthrene is affected by the type and origin of organic matter (Cassini et al., 1988; Budzinski et al., 1995). Precursors of alkyl phenanthrene are diterpenoids, e.g. abietane

and pimarane. One of the precursors for 1,7-DMP (pimanthrene) is 1-methyl-7-isopropylphenanthrene (retene: Simoneit et al., 1986) from conifers as well as vascular plants producing mainly type III kerogen (Wakeham et al., 1980; Radke et al., 1982b; Simoneit et al., 1986; Budzinski et al., 1995; Younker et al., 2012). Szczerba and Rospondek (2010) reported that both 1-MP and 2-MP can be generated by partial demethylation of 1,7-DMP in the matured stage of diagenesis. 1,7-DMP is generally abundant in the middle part of the core GDH-40, and decreases in the lower part, and 1,7-DMP is more abundant in the coals than in the coaly shales (Table 2). Figure 5c also shows many of the coals are rich in 1,7-DMP. Fabiańska et al. (2013) showed that retene, which is one of the possible source of 1,7-DMP, increases with maturity between R_o 0.6 to

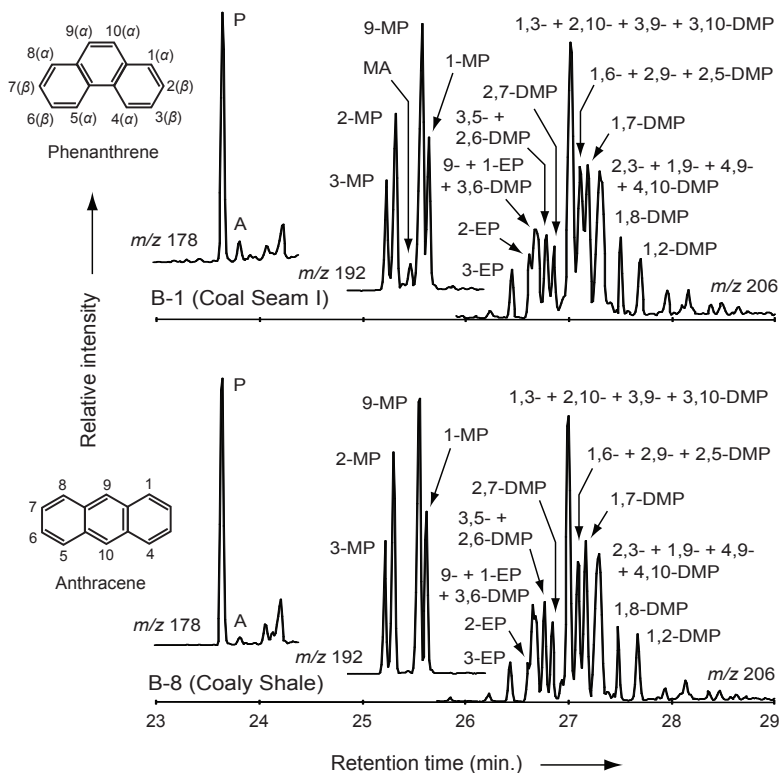


Fig.3. Representative m/z 178, 192 and 206 mass chromatograms for phenanthrene (P), anthracene (A), methylphenanthrenes (MP), methylanthracene (MA), ethylphenanthrenes (EP) and dimethylphenanthrenes (DMP) of Permian coals and coaly shales, Barapukuria Basin, NW Bangladesh.

0.8%. Retenes are commonly derived from conifers, and form as aromatization products of abietic acid and other diterpene derivatives (e.g. Laflamme and Hites, 1978). The retene is probably derived from resinous matter of gymnosperm vascular plants (Wakeham et al., 1980; Laflamme and Hites, 1978) and/or microbial sources (Jiang et al., 1998). Therefore, the 1,7-DMPs could possibly originate from gymnosperm resin.

In addition, anthracene (A) and methylanthracene (MA) is considerably more abundant in the coals than in the coaly shales (Fig.3 and Table2). A and MA are normally enriched in coals (Hughes and Dzou, 1995) or carbonaceous sediments, particularly in type III kerogen (Radke et al., 1982b; Garrigues et al., 1988). Similarly, $A/(A+P)$ and MA/MP are generally higher in coals than in coaly shales (Figs. 5d, e). Even though the coaly shales were closely accompanied by each coal seam (Fig.2), $A/(A+P)$ and MA/MP are clearly

different between them (Figs. 5d, e and Table3). A is usually less stable than P during diagenesis (Stout and Emsbo-Mattingly, 2008) and very low $A/(A+P)$ is in the coaly shale due to preferential loss of A during weathering (Yunker et al., 2002). Oxidative attack on aromatic ring carbons and oxidation of the alkyl carbons are of two pathways for aerobic degradation of alkyl aromatic hydrocarbons (Huang et al., 2004). Islam et al. (2004) reported that the Barapukuria Basin Gondwana coals are characterized by predominance of pteridosperms (ferns) including glossopterid, other types of pteridophytic plants, and coniferous gymnosperms. Therefore, the above characterization may be related to these coniferous gymnosperms and pteridosperms.

P and MP may originate also from pentacyclic triterpenoids or steroids (Streibl and Herout, 1969). High abundances of 1-MP are common in terrestrial sources organic matter, and 9-MP is relatively abundant both

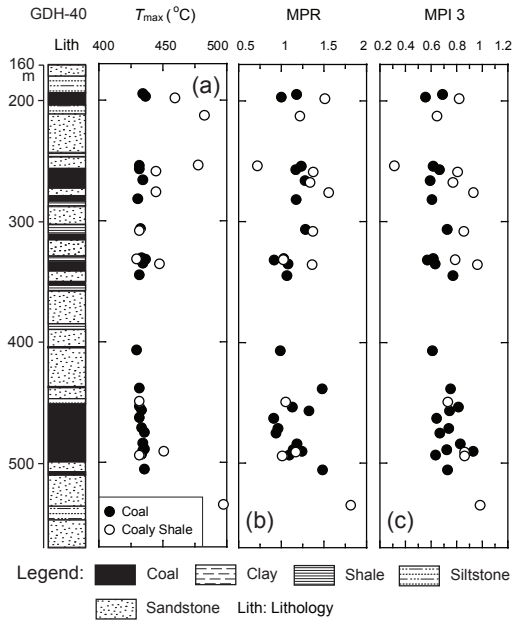


Fig. 4. Vertical distribution of T_{max} ($^{\circ}\text{C}$), MPR and MPI 3 of Permian coals and coaly shales, Barapukuria Basin, NW Bangladesh.

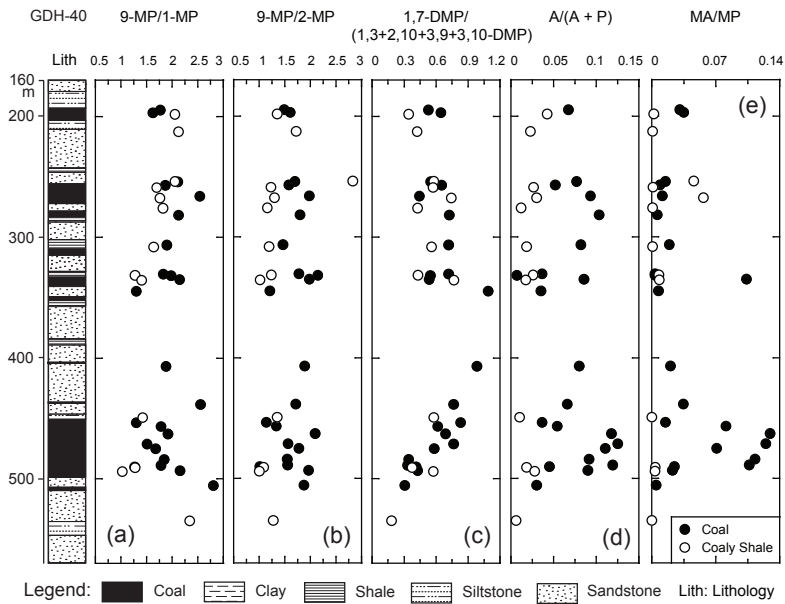


Fig. 5. Vertical distribution of (a) 9-MP/1-MP, (b) 9-MP/2-MP, (c) 1,7-DMP/(1,3+2,10+3,9+3,10-DMP), (d) A/(A+P) and (e) MA/MP of Permian coals and coaly shales, Barapukuria Basin, NW Bangladesh.

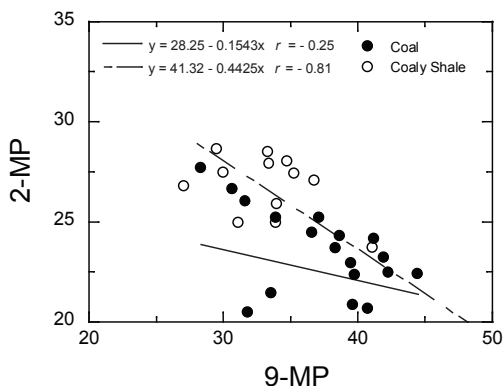


Fig. 6. Relationship between 9-MP and 2-MP of Permian coals and coaly shales, Barapukuria Basin, NW Bangladesh. Solid line is regression fitted to the combined data for coals and dashed line is regression for coaly shales.

in land plant and marine sources (Budzinski et al., 1995, 1997). However, immature coal and carbonaceous shales have substantially high 9-MP relative to 1-MP (Radke et al., 1982a), and it is over 2-MP and 3-MP. Therefore, the higher values of 9-MP/1-MP and 9-MP/2-MP ratios in the coals (Figs. 5a, b) are also ascribed to be terrestrial origin of organic matter such as coniferous gymnosperms and pteridophytic plants. This result is not conflict with the study of Khan et al. (2000) and Alexander et al. (1992), and suggested that 1,7-DMP/1,3- + 2,10- + 3,9- + 3,10-DMP ratio values ≤ 0.35 are considered to be derived from pteridosperms or glossopteris pteridosperms. The 1,7-DMP/1,3- + 2,10- + 3,9- + 3,10-DMP values range between 0.19 to 1.09 (Fig. 5c and Table 3), indicating a variable organic matter sources and/or floral changes in and around the peat bogs.

5. Summary and conclusions

Overall P, MP and DMP distributions in several sets of the Barapukuria coals and coaly shales shows different characteristics as follows:

(1) The MPR and MPI 3 values of the coaly shales are about 0.1 higher than those of the coals, although maturity based on T_{\max} (430-440°C) in the coals consistently shows early stage of oil generation. Average MPI

3 values are 0.69 ± 0.09 (coals, $n=23$) and 0.80 ± 0.17 (coaly shales, $n=13$), and average MPR values are 1.15 ± 0.16 (coals, $n=23$) and 1.28 ± 0.28 (coaly shales, $n=13$), respectively.

(2) Both 9-MP/1-MP and 9-MP/2-MP ratios in the coals are higher than in the coaly shales, and this could be due to an activated methylation to 9 position of P in the coals during early stage of oil generation. In addition, preferential biodegradation of MP in the peats, and conifer rich sources in the coals also may promote to increase the ratios in the coals. A negative correlation exists between 9-MP and 2-MP ($2\text{-MP} = -0.354 \times 9\text{-MP} + 36.6$, $r = -0.53$).

(3) 1,7-DMP (pimanthrene) from gymnosperm was generally more abundant in the coals than in the coaly shales.

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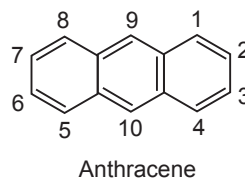
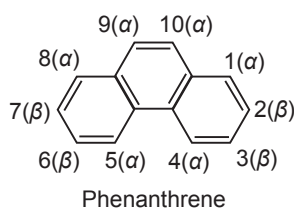
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Appendix A. 1. Structures of phenanthrene and anthracene,
2. Definition of parameters.

A.1. Structures of phenanthrene and anthracene.



A.2. Definition of parameters.

$$\text{MPR} = \frac{[2 - \text{MP}]}{[1 - \text{MP}]}$$

$$\text{MPI} 3 = \frac{[2 - \text{MP}] + [3 - \text{MP}]}{[1 - \text{MP}] + [9 - \text{MP}]}$$

$$\text{DMPR} = \frac{[2,6 - \text{DMP}] + [2,7 - \text{DMP}] + [3,5 - \text{DMP}]}{[1,3 - \text{DMP}] + [1,6 - \text{DMP}] + [2,5 - \text{DMP}] + [2,9 - \text{DMP}] + [2,10 - \text{DMP}] + [3,9 - \text{DMP}] + [3,10 - \text{DMP}]}$$