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Identification and distribution of pyrene, methylpyrenes and their isomers in rock extracts and crude oils

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ABSTRACT

Pyrene (Py), its alkylated homologues, fluoranthene (Fla), benzo[*a*]fluorene (B*a*F) and benzo[*b*]fluorene (B*b*F) have been unequivocally identified in crude oils and sedimentary rocks by co-injection with authentic standards and comparison of retention indices with those reported in the literature. The distribution patterns of pyrene, its C_1–C_2 alkyl derivatives and their isomers were then investigated in oils and sedimentary rocks with Early Paleozoic and Cenozoic origins. The oil groups of Ordovician–Cambrian reservoirs in the cratonic region of the Tarim Basin (NW China) are distinguished on the basis of the distribution patterns of pyrene, fluoranthene and their methylated homologues. The majority of the oil accumulations are characterized by low concentrations of fluoranthene and methylfluoranthenes relative to pyrene and methylpyrenes, respectively. In contrast, oils from wells TD2, TZ26, TZ162 and TZ451 have relatively higher concentrations of fluoranthene and methylfluoranthenes, indicating different origins. The distribution patterns of methylpyrenes in Cenozoic lacustrine shales from the Liaohe Basin (East China) show effects of maturity, where the 2-/1-MPy and MPYR (2-MPy/(2-MPy + 1-MPy)) ratios display a regular increase with increasing maturity. This study shows that pyrene, its alkylated homologues and their isomers are useful molecular markers in petroleum geochemistry and that the 2-/1-MPy and MPYR ratios are potential maturity indicators.

1. Introduction

Pyrene, its alkylated homologues and isomers are important four ring polycyclic aromatic hydrocarbons (PAHs) in crude oils and sedimentary rocks. The study of pyrene and methylpyrenes dates back more than half a century (Schnurmann et al., 1953). Pyrene, fluoranthene, benzo[*a*]fluorene and benzo[*b*]fluorene (see Fig. 1 for structures) were previously detected in coal tars, tire combustion fire residues, crude oils and sediments (McKay and Latham, 1973; Popl et al., 1974; Benner et al., 1990). Acephenanthrylene, another isomer of pyrene and fluoranthene (Fig. 1), is less thermodynamically stable and present at low concentrations or under the detection limit in the gas chromatography–mass spectrometry (GC–MS) analyses of oils and sedimentary rocks, but these three isomers are expected to be produced in most combustion processes of biomass and fossil fuels (Lee et al., 1977; Yunker et al., 2002). Pyrene (Py), the methylpyrenes (MPy) and fluoranthene (Fla) have potential toxicity, carcinogenicity and mutagenicity (Jacob et al., 1986; Mortelmans et al., 1986; Pahlman and Pelkonen, 1987). These compounds have been used as indicators for monitoring wastes contaminated with PAHs (Gschwend and Hites, 1981).

Two genetic types of PAHs occur in recent sediments. One group of PAHs, including pyrene and fluoranthene, is derived from combustion of organic materials such as fossil fuels and plant materials or pyrolytic PAHs (Jiang et al., 1998). The second group is considered to be derived from the diagenetic or catagenetic alteration of biological precursors (Laflamme and Hites, 1979; Jiang et al., 1998). PAHs including pyrene were also synthesized from benzene by impact shock waves in laboratory experiments (Mimura, 1995), which suggests that PAHs may be present in the interstellar medium, in atmospheres of Jovian planets and in carbonaceous chondrites. Grice et al. (2009) thought that pyrene and its isomers may be derived from microbial metabolism of fungi, higher plants or insects.

However, little work has been previously done on the systematic identification and geochemical application of pyrene, alkyl pyrenes and their isomers in rock extracts and crude oils. Early work by Lee et al. (1979) and Vassilaros et al. (1982) reported the retention indices for the methylpyrenes, benzofluorenes and two dimethylpyrenes, but some have proved not to be correct (Yunker et al., 2014). A different elution order for the methylpyrenes was subsequently presented by Radke et al. (1982a), but the

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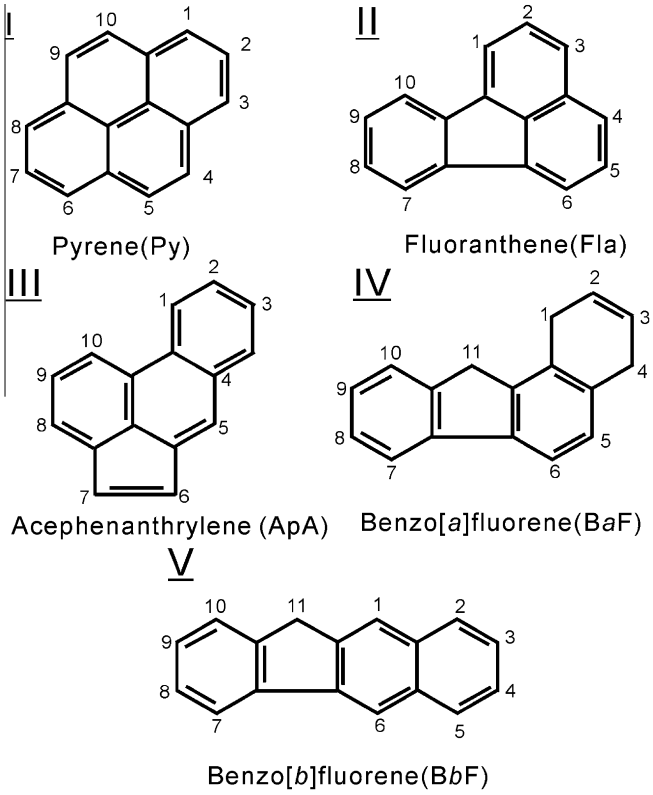

Fig. 1. Structure of the pyrene and benzofluorene isomers discussed in the text.

identifications and retention times were only tentative without co-injection of authentic standards. Garrigues et al. (1988) identified three methylpyrene isomers in coal extracts from the Mahakam delta, but analyses were based on high resolution spectroscopy (HRS). Kruge (2000) then identified and quantitated pyrene and three methylpyrene compounds by GC–MS, but there was no mention of standards and standard retention indices were not reported. Recently, Yunker et al. (2014) firmly identified the three methylpyrenes, several methylfluoranthenes and two benzofluorenes by co-injection of authentic standards and comparison of retention indices with those in the literature.

It is generally accepted that the isomers with methyl substitution on β-positions (more "externally" located) are more stable than those on α-positions of methylated PAHs (Radke, 1987). The isomers of methylated PAHs with the most thermodynamically stable substitution on β-positions are favored by the natural thermal maturation process (Radke et al., 1982a,b; Mackenzie and McKenzie, 1983; Alexander et al., 1985; Garrigues et al., 1988). Ratios of alkylated PAHs with isomers having a high degree of β-substitution to those with a high degree of α-substitution are sensitive to the changes of thermal maturity (Alexander et al., 1985).

Although the thermodynamic stabilities of alkyl pyrene isomers have not been calculated yet, the stability order of these three methyl isomers can be reasonably estimated. The most stable isomer among all methylpyrenes is expected to be the β-substituted 2-MPy and several maturity indicators with 2-MPy in the numerator have been proposed in previous studies, such as $MPyI_1$ ($3 \times$ 2-Mpy/(1-MPy + 4-MPy + Py)), $MPyI_2$ (2-MPy/(1-MPy + 4-MPy)) (Garrigues et al., 1988) and MPYR (2-MPy/(2-MPy + 1-MPy)) (Kruge, 2000). However, 2-MPy (β-substituted) makes the smallest contribution to a set of immature coal extracts from the Mahakam Delta (Indonesia), while 4-MPy (α-substituted) is the most prominent compound among the isomer series (Garrigues et al., 1988). The relative concentrations of the 1-MPy, 2-MPy and 4-MPy isomers show an irregular trend with increasing burial depth within immature to marginally mature stages and in many samples, the $MPyI_2$ ratio only varies over small ranges (Garrigues et al., 1987; Garrigues et al., 1988). For this reason, the maturity indicators $MPyI_1$ and $MPyI_2$ have not been widely applied in the maturity assessment of oils and sedimentary organic matter.

In this paper, we firmly identify a series of methylpyrenes, isomers of methylfluoranthenes, benzo[*a*]fluorene and benzo[*b*]fluorene (*m*/*z* 216) and C_2 alkyl pyrenes (*m*/*z* 230) in crude oils and rock extracts by co-injection of authentic standards in GC–MS analyses and the comparison of retention indices (*I*) with those previously reported. The distribution patterns of methylpyrenes, methylfluoranthenes, benzo[*a*]fluorene and benzo[*b*]fluorene and

Table 1
The absolute concentrations of pyrene, methylpyrene isomers and related parameters for sedimentary rocks from well SG1, Liaohe Basin, East China.

Sample No.	Depth (m)	TOC (%)	T_{max} (°C)	*Ro* (%) mean	HI	OI	Pyrene (μg/g C_{org})	2-MPy (μg/g C_{org})	4-MPy (μg/g C_{org})	1-MPy (μg/g C_{org})	2/1-Mpy	4/1-MDBT	MPYR	MPyI1	MPyI2	Fla/(Fla + Py)	MFla/(MFla + MPy)
SG04	2314	1.37	432	0.36	172	100	29.4	1.37	2.02	1.44	0.95	1.76	0.49	0.13	0.40	0.64	0.26
SG05	2352	1.44	435	0.36	164	93	7.75	0.81	1.51	0.80	1.01	1.68	0.50	0.24	0.35	0.69	0.26
SG06	2404	1.72	433	0.33	235	73	8.26	0.53	0.71	0.42	1.28	1.73	0.56	0.17	0.47	0.63	0.31
SG07	2449	1.93	431	0.32	329	52	44.9	1.50	2.29	1.55	0.96	1.24	0.49	0.09	0.39	0.34	0.25
SG08	2484	2.24	430	0.33	356	53	3.43	0.40	0.62	0.46	0.87	1.28	0.47	0.27	0.37	0.71	0.31
SG09	2518	2.11	430	0.33	409	61	6.51	0.39	0.58	0.42	0.92	1.59	0.48	0.16	0.39	0.60	0.28
SG11	2653	1.83	433	0.34	296	83	9.82	0.71	1.10	0.69	1.03	1.85	0.51	0.18	0.40	0.63	0.31
SG12	2672	1.92	434	0.44	391	75	9.86	2.39	3.25	1.90	1.26	1.99	0.56	0.48	0.46	0.54	0.17
SG13	2730	1.91	434	0.45	359	83	25.1	5.10	5.88	3.36	1.52	2.69	0.60	0.45	0.55	0.39	0.18
SG14	2783	1.86	435	0.52	354	120	9.88	2.89	4.17	2.30	1.26	2.14	0.56	0.53	0.45	0.56	0.19
SG15	2815	1.9	434	0.47	336	74	29.0	4.23	5.18	2.87	1.47	2.56	0.60	0.34	0.53	0.48	0.22
SG16	2888	1.76	435	n.d.	354	78	14.6	5.74	6.74	3.96	1.45	2.61	0.59	0.68	0.54	0.44	0.17
SG17	2914	1.78	437	0.49	312	56	18.5	5.02	6.13	3.33	1.51	2.64	0.60	0.54	0.53	0.43	0.16
SG18	2956	1.77	437	0.44	298	99	15.3	4.77	5.76	3.12	1.53	2.26	0.60	0.59	0.54	0.40	0.19
SG19	3111	2.13	437	0.61	345	80	21.7	8.51	10.3	5.93	1.43	2.43	0.59	0.67	0.53	0.43	0.16
SG20	3239	1.99	437	0.61	319	91	1085	55.6	49.2	32.9	1.69	2.88	0.63	0.14	0.68	0.57	0.32
SG21	3304	3.27	435	0.58	274	64	1834	113	105	76.6	1.48	2.89	0.60	0.17	0.62	0.60	0.32
SG22	3372	1.87	439	0.59	294	86	1266	59.9	57.2	35.6	1.68	2.99	0.63	0.13	0.65	0.50	0.29
SG25	3752	1.72	441	0.65	233	108	1193	88.7	78.6	50.6	1.75	3.79	0.64	0.20	0.69	0.68	0.36
SG26	3819	1.64	439	0.68	213	122	1324	78.8	69.3	40.1	1.97	3.74	0.66	0.16	0.72	0.64	0.37
SG27	4052	1.42	440	0.73	202	113	557	34.2	37.3	21.3	1.61	4.40	0.62	0.17	0.58	0.60	0.29

Note: MPy: methylpyrene; MDBT: methyldibenzothiophene; MPyI1: $3 \times$ 2-Mpy/(1-MPy + 4-MPy + Py), MPyI2: 2-MPy/(1-MPy + 4-MPy); MPYR: 2-MPy/(2-MPy + 1-MPy).