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A New Parameter for Maturity Assessment of Organic Materials in Sediments Based on Thermal Isomerization of Monomethylphenanthrenes

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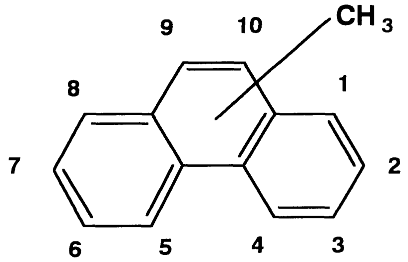
Monomethylphenanthrenes(MPs) were isomerized by heating in the presence of Na-montmorillonite to give a mixture of four isomers (1-, 2-, 3-, and 9-MP). The ratio of 1- and 2-MP produced from each isomer reached a constant value after appropriate time of heating. This ratio provides a new parameter for maturity assessment of sedimentary organic materials.

Polycyclic aromatic hydrocarbons (PAHs), e.g., naphthalene, phenanthrene, are widely distributed in sedimentary rocks and are common constituents of petroleum. Nonaromatic polycyclic compounds of biological origin such as steroids and triterpenoids are now considered to be aromatized by heat or pressure or by catalytic action of minerals in sediments to produce PAHs.[1,2] Alkylated PAHs thus produced have undergone isomeric rearrangement and dealkylation reactions in sediments, resulting in their distribution in sediments and petroleum with characteristic compositions of their isomers and homologs. The observed isomer composition patterns of methyl or dimethyl derivatives of naphthalene or phenanthrene have been utilized as parameters of the maturities of sedimentary organic materials.[3-7] We now propose a new parameter for the maturity determination on the basis of the thermal isomerization reaction of methylphenanthrenes in the presence of Na-montmorillonite.

The substrates employed for the rearrangement reaction were 1-, 2-, 3-, and 9-methylphenanthrene (MP). The 4-methyl isomer was also used as an authentic sample for gas chromatographic analysis, but it was not formed in the reaction stated here. Each isomer (1 mg) was heated with Na-montmorillonite (40 mg) in a degassed sealed glass tube at 250, 300, 350, or 400 °C. Control experiments were performed without Na-montmorillonite at 500 °C for 24 h using the four isomers. The products were then extracted with a benzene-methanol (4:1) mixture and analyzed by gas chromatography and gas chromatography-mass spectrometry.



Monomethylphenanthrene

Figure 1 shows the results of the control experiments. Almost all quantities of the starting materials survived without any detectable formation of isomerization products under the drastic conditions, except trace amounts of a demethylated product, phenanthrene. On the other hand, in the presence of Na-montmorillonite each isomer of the MPs smoothly underwent the rearrangement to produce a mixture of 1-, 2-, 3-, and 9-MP as shown in Fig. 2. The 4-methyl isomer was not formed probably due to its instability based on a steric repulsion between the methyl group and a proton at the 5-position. These results show that Na-montmorillonite catalyzed the thermal isomerization of MPs, which is a reversible reaction. Figure 2 also represents the formation of phenanthrene and di- and trimethyl-phenanthrenes, which was confirmed by mass fragmentographic analysis of the reaction mixture as well, indicating that a demethylation and an intermolecular methyl-transfer reaction also took place simultaneously in the reaction system. Higher temperatures seem to favor the generation of phenanthrene. Another reason for the decrease of total amounts of methylphenanthrenes would be their carbonization caused by high temperatures and catalytic action of the clay mineral, since the mineral turned dark gray or black after heating.

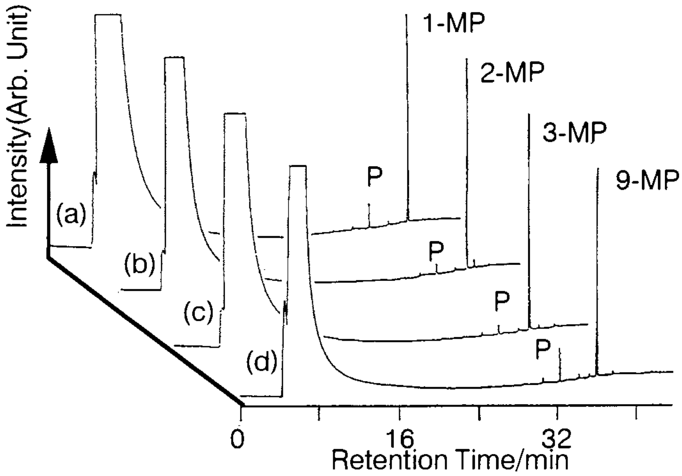


Fig. 1. Gas chromatograms of products of control experiments using (a)1-, (b)2-, (c)3-, and (d)9-MP (P: phenanthrene).
GC conditions: OV-1701 column(50m x0.25mm i.d.), 90 °C-130 °C at 10 °C/min,130 °C-250 °C at 4 °C/min.

Examination of the results in Table 1 shows that the ratio (R_{12} = 1-MP/(1-MP + 2-MP) of 1- and 2-MP produced from the four isomers converged to definite values (R^{e}_{12}) at all the temperatures employed here (Table 2). The R_{12} ratio became practically constant after 24 to 48 h at 300 °C and within 6 h at both 350 °C and 400 °C. On the other hand, the isomerization revealed too slow to give the R^{e}_{12} values on the heating at 250 °C. There could be, however, two possible ways to estimate R^{e}_{12} at 250 °C from the present data. One is to obtain R^{e}_{12} from the average value (0.190) of the four R_{12} values at 72 h. The other way is to adopt the R_{12} value of 9-MP at 72 h as R^{e}_{12} at 250 °C. Since R_{12} values of 9-MP showed no heating time dependence at each temperature, we chose the latter to determine the value at 250 °C as 0.186. It is a remarkable feature of

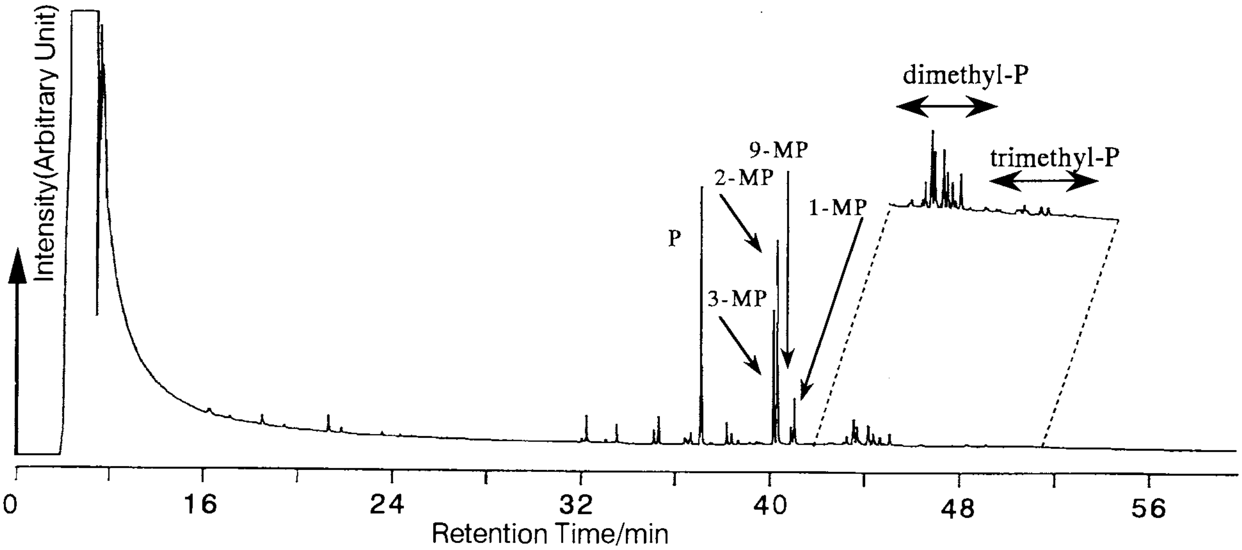


Fig. 2. Gas chromatograms of products of a heating experiment of 1-methylphenanthrene with Na-montmorillonite at 250 °C for 72 h.
GC conditions and abbreviation are the same as stated in the legend of Fig. 1.

Table 1. Products(mcg) of thermal isomerization of methylphenanthrenes

	Temperature: 250 °C									
	Substrate: 1-MP					2-MP				
Time/h	1-MP	2-MP	3-MP	9-MP	P	1-MP	2-MP	3-MP	9-MP	P
12	80.7	125	29.5	4.47	143	27.4	201	23.2	2.39	76.1
24	28.9	73.8	26.4	3.80	76.2	17.4	96.5	27.1	2.99	62.1
36	23.1	67.5	27.2	3.94	73.5	12.5	61.7	24.6	3.91	51.9
48	15.7	55.2	27.6	4.06	65.5	13.1	66.3	26.1	3.07	54.8
72	11.1	42.6	23.9	3.62	52.4	8.32	34.3	21.3	4.50	37.2
	3-MP					9-MP				
	1-MP	2-MP	3-MP	9-MP	P	1-MP	2-MP	3-MP	9-MP	P
12	6.43	30.4	139	8.12	87.8	6.07	26.5	36.3	63.3	124
24	10.2	38.3	86.5	10.9	77.0	5.34	23.4	28.8	36.7	92.3
36	5.57	27.0	45.1	6.28	54.8	4.83	21.6	25.4	27.3	79.4
48	5.09	23.9	33.5	5.41	45.0	4.86	21.6	24.6	25.7	74.1
72	4.81	23.2	28.0	5.20	42.5	4.25	18.6	19.9	19.0	58.9
	Temperature: 300 °C									
	Substrate: 1-MP					2-MP				
Time/h	1-MP	2-MP	3-MP	9-MP	P	1-MP	2-MP	3-MP	9-MP	P
6	42.4	106	42.3	15.7	119	19.1	80.8	27.2	9.73	81.9
24	24.5	83.1	42.3	12.4	110	9.89	38.5	22.6	7.27	58.2
48	13.8	49.8	31.3	9.29	70.4	8.21	31.2	22.1	7.37	49.8
72	11.0	41.3	29.4	9.60	72.5	7.44	28.1	22.2	7.72	56.1
	3-MP					9-MP				
	1-MP	2-MP	3-MP	9-MP	P	1-MP	2-MP	3-MP	9-MP	P
6	8.56	30.2	93.6	15.3	94.4	10.3	39.7	50.1	72.3	135
24	6.98	26.8	39.3	11.2	68.0	10.6	40.6	48.6	52.7	133
48	5.17	19.4	22.3	7.59	44.0	7.43	28.3	31.9	27.4	79.6
72	6.21	23.5	31.1	9.83	59.1	7.74	29.3	32.2	26.3	86.7
	Temperature: 350 °C									
	Substrate: 1-MP					2-MP				
Time/h	1-MP	2-MP	3-MP	9-MP	P	1-MP	2-MP	3-MP	9-MP	P
6	23.4	74.5	41.4	15.4	117	15.6	55.1	28.2	11.4	88.6
12	14.6	51.9	34.8	11.8	94.3	14.7	49.4	34.5	12.4	91.8
18	14.0	45.6	30.4	10.7	83.5	15.8	52.3	35.0	13.0	90.8
	3-MP					9-MP				
	1-MP	2-MP	3-MP	9-MP	P	1-MP	2-MP	3-MP	9-MP	P
6	9.98	32.8	66.0	17.6	100	12.3	40.1	49.1	60.6	135
12	10.4	37.6	62.3	15.0	103	9.00	30.9	34.8	31.7	99.8
18	10.7	38.1	52.9	15.3	94.4	10.4	35.8	39.1	31.6	112
	Temperature: 400 °C									
	Substrate: 1-MP					2-MP				
Time/h	1-MP	2-MP	3-MP	9-MP	P	1-MP	2-MP	3-MP	9-MP	P
3	33.6	95.7	45.3	19.2	135	28.7	88.5	42.1	16.2	123
6	27.5	86.4	47.8	17.7	143	28.2	88.8	53.6	20.4	153
12	26.5	84.1	47.9	18.3	148	28.6	89.8	45.6	17.8	143
	3-MP					9-MP				
	1-MP	2-MP	3-MP	9-MP	P	1-MP	2-MP	3-MP	9-MP	P
3	11.5	36.8	105	17.5	117	14.3	45.5	47.7	62.8	144
6	13.9	44.5	90.7	19.7	133	14.7	43.8	49.8	50.1	149
12	13.6	42.5	88.9	20.2	133	14.5	45.1	52.2	58.1	155

the isomerization of 9-MP that 1- and 2-MP produced are in equilibrium with each other at the early stage of heating, as is clealy shown in the results of the heating experiments at 250 °C and 350 °C (Table 2). An approximately linear relationship exists between the R^{e}_{12} value and the temperature applied to the MPs as shown in Fig. 3. It seems reasonable that higher temperatures favored the generation of 1-MP, which is less stable than 2-MP.

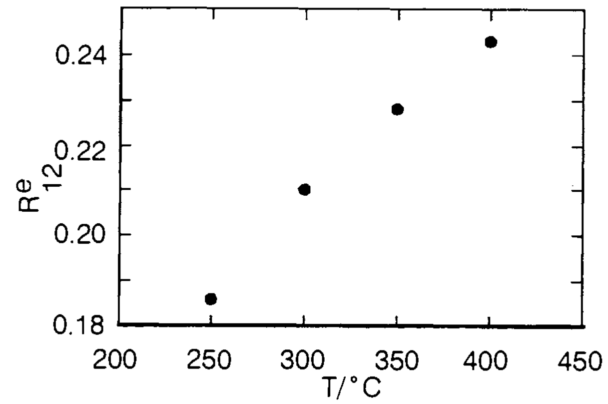


Fig. 3. Plots of R^e_{12} against temperature (T).

Although R^e_{12} values of MPs in sediments or petroleums might be affected by kind of clay mineral catalysts, source type of MPs, water content of sediments, etc., and different from those obtained in this experiment, R_{12} value of MPs in nature is expected to change toward R^e_{12} with time. The new parameter R_{12} requires the determination of only two isomers of MPs in sediments. Therefore, the ratio of 1- and 2-MP provides a useful additional parameter for maturity assessment of sedimentary organic matters.[8]

Table 2. R_{12} values of 1-, 2-, 3-, and 9-methylphenanthrenes

Temperature: 250 °C

Substrate Time/h	1-MP	2-MP	3-MP	9-MP
12	0.392	0.120	0.175	0.186
24	0.282	0.153	0.210	0.186
36	0.255	0.168	0.171	0.183
48	0.221	0.165	0.176	0.184
72	0.206	0.195	0.172	0.186

R^e_{12}: 0.186(R_{12} of 9-MP at 72 h)

Temperature: 300 °C

Substrate Time/h	1-MP	2-MP	3-MP	9-MP
6	0.286	0.191	0.221	0.205
24	0.228	0.204	0.206	0.206
48	0.218	0.208	0.210	0.208
72	0.211	0.209	0.209	0.209

R^e_{12}: 0.210(the mean of R_{12} at 72 h)

Temperature: 350 °C

Substrate Time/h	1-MP	2-MP	3-MP	9-MP
6	0.234	0.221	0.233	0.233
12	0.220	0.229	0.217	0.226
18	0.234	0.232	0.219	0.225

R^e_{12}: 0.228(the mean of R_{12} at 18 h)

Temperature: 400 °C

Substrate Time/h	1-MP	2-MP	3-MP	9-MP
3	0.260	0.242	0.239	0.239
6	0.242	0.241	0.238	0.250
12	0.240	0.242	0.242	0.243

R^e_{12}: 0.242(the mean of R_{12} at 12 h)

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8) The following table shows R_{12} values of sediments of the Shinjo basin, northeastern Japan. In this case, the value decreased with increasing depth, indicating increasing maturity of sedimentary organic matters. The details will be reported elsewhere.

Sample No.	Relative Depth/m	R_{12}
83106	0	0.587
83103	250	0.500
90101	850	0.441
90103	1250	0.439

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