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A New Parameter for Maturity Determination of Organic Matter in Sediments Based on the Clay-Catalyzed Thermal Isomerization of Monomethylphenanthrenes

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Monomethylphenanthrenes (MPs) were isomerized by heating in the presence of Na-montmorillonite at 250—400 °C. Isomerization between 1- and 2-MP was found to proceed faster than those between the other sets of MPs. On the basis of this facile interconversion, the molar ratio of 1- to 2-MP was suggested to be a useful new parameter for the maturity assessment of sedimentary organic matter. This parameter was tested in a geochemical study on Miocene to Pliocene sediments in the Shinjo basin of Yamagata Prefecture. We determined the molar ratio in 12 depth-differing sediments, and found an almost linearly decreasing trend in the ratio with increasing depth, showing a good correlation of this parameter to the maturity of the sedimentary organic matter.

Many challenging investigations had been successfully attempted to relate the chemical properties or features of compounds found in nature to their histories. One of the well-known examples is the radiocarbon dating of ancient organic matter, while the contents of the stable carbon isotopes in carbonaceous sediments can distinguish matters of biological origin.[1] The radioisotope clocks applicable to older samples utilize isotopes with a long lifetime, such as ^{87}Rb, ^{235}U, and ^{238}U, and determined the ages of meteorites, the moon rock and the oldest sediments on the earth.[2—5] The ages of fossils or ancient sediments were also estimated from their contents of D-amino acids produced by the racemization of L-amino acids.[6,7] The distribution of individual hydrocarbons in crude oils can provide information on the level of maturity, which represents their time–temperature history. For example, the carbon preference index that describes the odd-over-even carbon number preference in *n*-alkanes resulting from higher plant waxes had been used for a maturity measurement.[8] In this paper, we propose a new parameter for the maturity determination of organic matter in sediments based on the thermal isomerization of methylphenanthrenes catalyzed by a clay mineral.

Polycyclic aromatic hydrocarbons are common constituents of ancient sediments, and have been considered to be derived partly from the aromatization of nonaromatic polycyclic compounds of biological origin, such as steroids and triterpenoids, by the heat and catalytic action of minerals in sediments.[9,10] Since thus-produced alkylated aromatic compounds have undergone an isomeric rearrangement and dealkylation reactions in sediments, the distribution patterns of these compounds reflect the extent of the thermal maturation experienced. Therefore, the relative abundances of methylated naphthalenes and phenanthrenes in sediments have been used to obtain information on the thermal maturity of sedimentary organic materials.[11—19] On the other hand, laboratory pyrolysis experiments of alkyl aromatic compounds in the presence of clay minerals have been performed to obtain maturity indicators based on isomer ratios,[20,21] because the minerals possess suitable acidic sites necessary to promote the isomerization reaction.

In the present study,[22] we performed clay-catalyzed thermal reactions of all the isomers of methylphenanthrenes (MPs), except for the least stable one (4-MP), over a temperature range of 250—400 °C to determine the isomeric rearrangement pathways and the product distributions. The time-course of the reactions was followed until their molar compositions reached a steady state. We then analyzed the MPs in Miocene to Pliocene sediments in order to obtain the distribution of MP isomers in the stratigraphic sequence and to relate them to the thermal maturity of organic matter in the sediments in terms of their molar ratios.

Experimental

Thermal Isomerization of Methylphenanthrenes. A solution (0.5 ml) of 1-, 2-, 3-, and 9-MP (1 mg) in benzene was shaken with Na-montmorillonite (40 mg) in a glass test tube for 5 min and lyophilized to dryness. After replacing the air in the test tube with argon, the tube was degassed and sealed. The glass tubes containing each isomer of MP and the clay were heated in an electric oven at 250, 300, 350, or 400 °C. At appropriate time intervals, the tube was opened and the clay was extracted under sonication with a mixture (1 ml) of benzene and methanol (4 : 1) for 30 min. After centrifugation, the supernatant was saved. The extraction was repeated ten times and the combined extract was used for the identification and quantification of phenanthrenes by a gas chromatograph coupled to a mass spectrometer (Shimadzu GCMS QP-1000A). Control experiments were performed without Na-montmorillonite at 500 °C for 24 h using the four isomers in a similar manner to that stated above.

The GC was equipped with an FS-WCOT OV-1701 bonded capillary column (50 m$\times$0.25 mm i.d.), and helium was used as a carrier gas. After sample injection, the oven temperature was held at 90 °C for 1 min, raised to 130 °C at a rate of 10 °C min^{-1}, and then to 250 °C at 4 °C min^{-1}. The mass spectrometer was scanned every 1.0 s over *m*/*z* 50—300 in the electron-impact ionization mode at 70 eV with the ion source temperature at 250 °C. The reaction products were identified by a comparison of their retention times on the gas chromatograms and of mass fragment patterns with those of standard compounds. The concentrations of phenanthrenes were estimated by the peak areas of molecular ions on mass fragmentograms.

Analysis of Methylphenanthrenes in Sediments. The sediment samples analyzed in this study are chiefly marine shales and mudstones of the Nakawatari and Noguchi Formations of Pliocene and of the Furukuchi and Kusanagi Formations of Late to Middle Miocene, in stratigraphically descending order.[23] They were collected at outcrops along the Oashizawa route in the Shinjo basin of the Yamagata Prefecture, northeastern Japan, in 1980 for a joint study of organic and inorganic constituents and their diagenesis.[23]

For each analysis, 1.0 g of powdered sample was extracted at room temperature with a 3 ml benzene/methanol (4 : 1) mixture by sonication. After centrifugation, the supernatant was saved. The benzene/methanol extraction and centrifugation processes were repeated ten times and the saved supernatants were combined. The combined solution was concentrated to about 1 ml in a stream of nitrogen, followed by separation on a silica gel column. Hexane was used to elute saturated hydrocarbons, benzene for the aromatic hydrocarbons, and methanol for the hetero-compounds. The aromatic fraction was concentrated in a stream of nitrogen while taking care to avoid complete evaporation; also, the volume of the concentrated solution was adjusted to 50 μl.

The identification and quantification of individual components in the aromatic fraction were carried out in a similar way as stated concerning the thermal reactions, except for a column used on gas chromatography. In this analysis, a fused-silica capillary column (60 m$\times$0.25 mm i.d.) coated with TC-1701 (GL Sciences Inc.) was used, and the oven temperature was programmed to give 90 °C for the initial 1 min, from 90 to 130 °C at a rate of 10 °C min^{-1}, from 130 to 210 °C at 2 °C min^{-1}, and from 130 to 250 °C at 4 °C min^{-1}.

To avoid any laboratory contamination, all glassware was preheated at 500 °C for at least 3 h, and organic solvents were doubly distilled.

Results and Discussion

Thermal Isomerization of Methylphenanthrenes Catalyzed by Na-Montmorillonite. The heating experiments of 1-, 2-, 3-, and 9-MP showed that isomerization reactions had taken place at 250, 300, 350, and 400 °C in the presence of Na-montmorillonite. As shown in Fig. 1, each isomer underwent a rearrangement to produce a mixture of all the isomers, except for 4-MP, although phenanthrene is one of the major products with dimethyl- and trimethylphenanthrenes as minor ones. The 4-methyl isomer was not found in all of the reactions performed, probably because of its instability

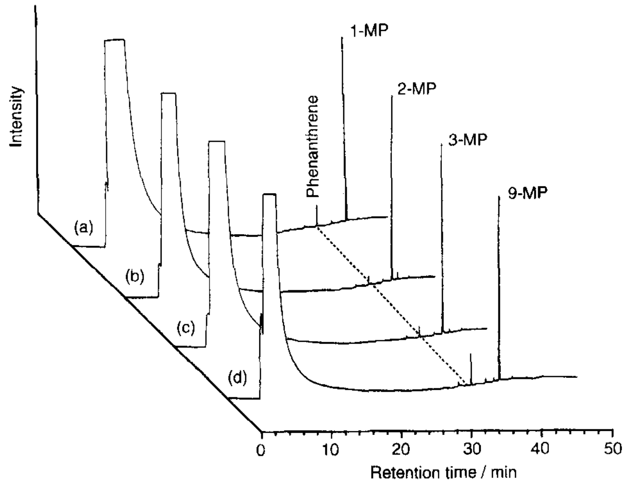

Fig. 2. Gas chromatograms of products of control experiments using (a) 1-, (b) 2-, (c) 3-, and (d) 9-methylphenanthrene (MP).

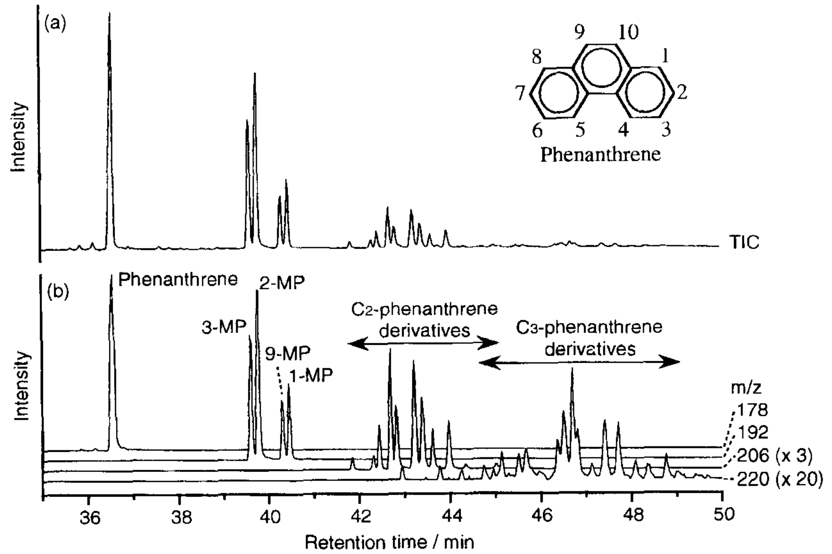

Fig. 1. Gas chromatograms of products of a heating experiment using 1-methylphenanthrene (1-MP) with Na-montmorillonite at 350 °C for 24 h. (a) Total ion chromatogram (TIC). (b) Mass fragmentograms.

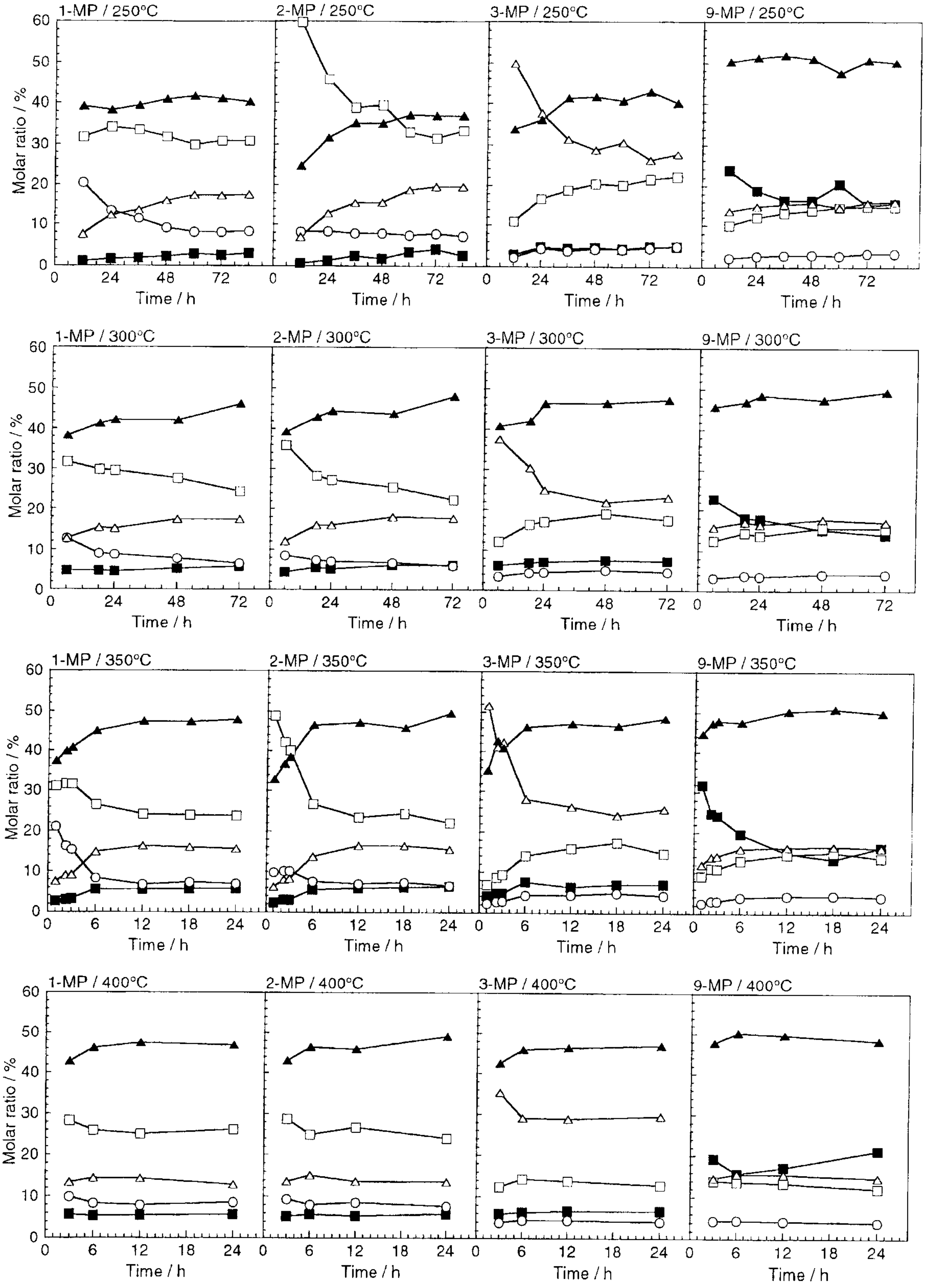

Fig. 3. Time-course plots of molar ratios of phenanthrene and methylphenanthrenes (MPs) produced in heating experiments using 1-, 2-, 3-, and 9-MP at 250, 300, 350, and 400 °C (▲: Phenanthrene, ○: 1-MP, □: 2-MP, △: 3-MP, ■: 9-MP).

based on a steric repulsion between the methyl group and a proton at the 5-position. The reaction of 4-MP was carried out only at 250 °C, resulting in a complete transformation to 3-MP and phenanthrene by 12 h. The subsequent time-course of the products was similar to that in the reaction of 3-MP. The total recoveries of phenanthrenes in the heat-

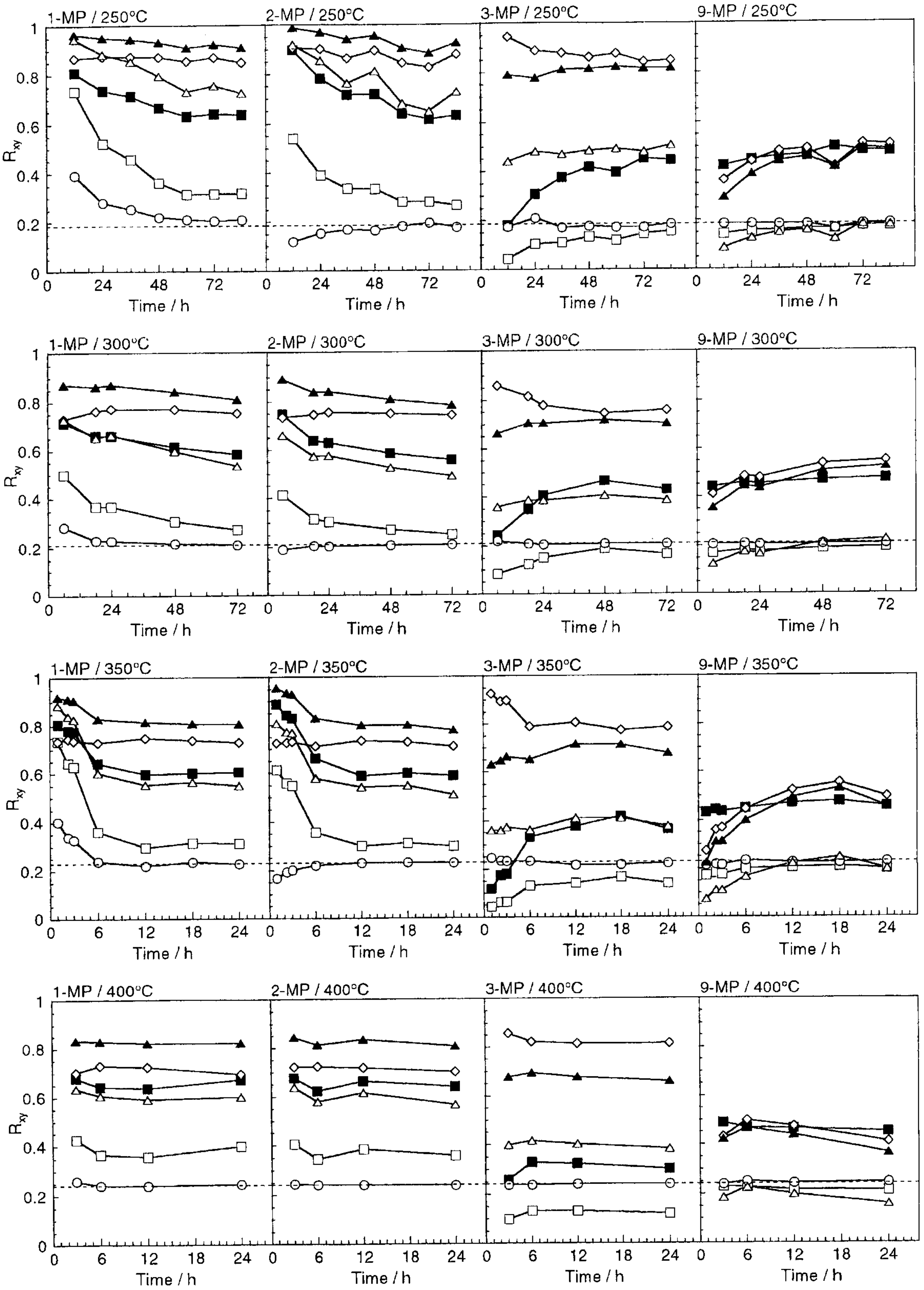

Fig. 4. Time-course plots of R_{xy} values obtained in heating experiments using 1-, 2-, 3-, and 9-methylphenanthrene (MP) at 250, 300, 350, and 400 °C (○: R_{12}, □: R_{13}, △: R_{19}, ■: R_{23}, ▲: R_{29}, ◇: R_{39}).

ing experiments were only 15—30% based on the substrate. Degradation and carbonization of phenanthrenes might have occurred by high temperatures and catalytic action of the clay mineral during the course of the reaction to give the low yields, as judged from an observation that the mineral turned gray after heating and the extracts from the reaction mixtures were colored yellow. On the other hand, control experiments involving the four isomers were performed in the absence of the clay mineral at 500 °C for 24 h, showing almost total recovery in quantity of the substrate without any detectable formation of isomerization products, but with trace amounts of phenanthrene, as illustrated in Fig. 2. These results clearly show that the Na-montmorillonite catalyzed the isomerization of MPs under the employed conditions, and that the surface of the glass tube used did not contribute to the reaction as a catalyst.

Figure 3 shows time-course plots of molar ratios of the substrates and products in the isomerization reaction. Changes in their molar compositions during the reaction at 250, 300, 350, and 400 °C terminated after 72, 48, 12, and 6 h, respectively. This would be attributed to the deactivation of the clay catalyst at the time when the ratios of MPs ceased to change during the reaction. The deactivation was further supported from the fact that the recoveries of the phenanthrenes remained constant after terminating the compositional changes at each temperature. However, the isomerizations of 1- and 2-MP were recognized to be a sufficiently rapid reaction to attain equilibrium before deactivation of the catalyst, as can be seen in Fig. 3.

A thermal reaction using 1-MP generated a larger amount of 2-MP than that of the starting isomer shortly after the beginning, followed by a decrease of the molar ratio of this product. 1-MP initially produced from 2-MP also had a tendency to decrease as the reaction proceeded, whereas the other MPs produced in these reactions gradually increased with time. These facts clearly show that 2- and 1-MP in the reactions of 1- and 2-MP, respectively, were produced prior to 3- and 9-MP. The final compositions of both 1- and 2-MP produced from 1-MP coincided with those from 2-MP at all of the reaction temperatures employed here. Therefore, the ratios (R_{12}) of 1- to 1- plus 2-MP produced from the isomerizations of 1- and 2-MP converged to definite values (R^{e}_{12}) at each temperature, as shown in Fig. 4, where R_{xy} is defined by

$$R_{xy} = \frac{[x\text{-MP}]}{[x\text{-MP}] + [y\text{-MP}]}, \quad \text{where } x \text{ and } y = 1, 2, 3, \text{ or } 9.$$

Also, R^{e}_{xy} represents R_{xy} at the equilibrium state of x- and y-MP. A facile interconversion of 1- and 2-methylnaphthalene was reported by the action of strong acids, such as anhydrous HF–BF$_3$, while migrations of a methyl group between the adjacent β–β as well as between the *peri* positions were known to proceed to a negligible extent in solution.[24] In contrast to the isomerization of methylnaphthalenes, the clay-catalyzed thermal reactions of MPs caused the interconversion of each isomer and the intermolecular methyl transfer leading to the formation of dimethylphenanthrenes to some extent, as can be seen in Fig. 1. The isomerization of 9-MP, which should bring about methyl migration between the *peri* positions, however, was observed to be a slow reaction, even at 400 °C, because the molar composition of the starting isomer decreased only to the levels of those of the more stable 2- and 3-MP produced. As is distinct from the reactions of 1- and 2-MP, the methyl shift from 9-MP afforded simultaneously 1-, 2-, and 3-MP in such proportions that seemed to be reasonable in view of thermodynamical stability, as shown in Fig. 3. This finding was supported from the facts that R_{12}, R_{13}, and R_{23} indicated steady values near to the initial stage, and especially the R^{e}_{12} values obtained in this reaction fairly coincided with those in the isomerizations of 1- and 2-MP at every reaction temperature. Therefore, R_{12}, R_{13}, and R_{23} obtained in the isomerization of 9-MP can be accepted as R^{e}_{12}, R^{e}_{13}, and R^{e}_{23}, respectively. For the same reason, the isomerization of 3-MP provided R^{e}_{12}, R^{e}_{19}, and R^{e}_{29} and those of both 1- and 2-MP did R^{e}_{39}. Thus, the constancy of the R_{xy} values was also observed for R_{12}, R_{19}, and R_{29} obtained in the reactions of 3-MP, and for R_{39} in those of 1- and 2-MP. The R^{e}_{12} values in the experiments using 3-MP again agreed with those obtained in the reactions using 1-, 2-, and 9-MP.

In conclusion, the interconversion of 1- and 2-MP proceeded fast enough to give the R^{e}_{12} value at every temperature. The other types of isomerization were slower than the above-mentioned reaction, but produced MPs in thermodynamical equilibrium with each other to afford the R^{e}_{xy} values. Heating experiments with a sufficient quantity of the clay catalyst would provide all kinds of R^{e}_{xy} values for the reactions of the four isomers, though a use of the increased quantity of the catalyst seems impractical because of a further decrease of the MPs recoveries with the heating time. Among the R^{e}_{xy} values shown in Fig. 5, only R^{e}_{12} was obtained from all of the reactions at each temperature. The R^{e}_{xy} values reflect the thermodynamical stability of each MP isomer, and show a slight, but reasonable, tendency to favor the generation of less-stable isomers at higher temperatures. Although the R^{e}_{xy} values in sediments might be affected by various environmental factors to afford different values from those obtained in this experiment, the R_{xy} values are expected to change toward R^{e}_{xy} with time. The change of the R_{xy} values to their equilibrium values (R^{e}_{xy}) reflects a maturation process of phenanthrenes in sediments; also, a difference between the R_{xy} value of a sample and the equilibrium value (R^{e}_{xy}) indicates the degree of maturity of the sample. Especially, the R_{12}

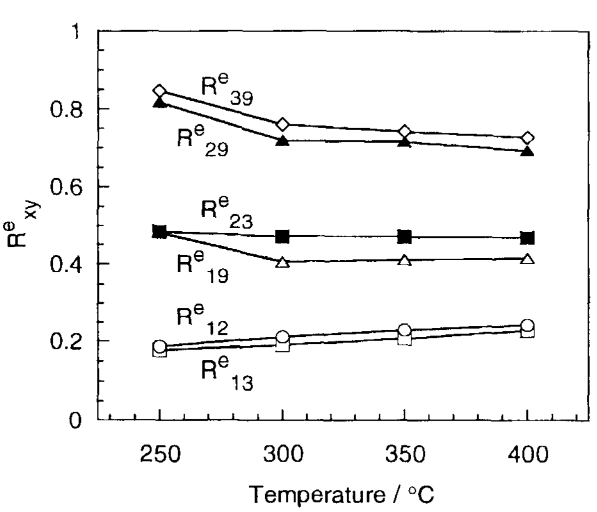

Fig. 5. Plots of R^{e}_{xy} values against temperature.

value is considered to be most useful for the maturity assessment of organic matter, even in younger sediments, because its remarkably faster attainment to equilibrium value provides the great sensitivity of this parameter to the thermal environment, as revealed in this investigation.

Maturity Assessment Study of Miocene to Pliocene Sediments. We analyzed 12 depth-differing sediments of Miocene to Pliocene over a 1600 m thick sequence in the Shinjo basin. We detected phenanthrene and methylphenanthrenes after the extraction of organic compounds from the sediments, followed by chromatographic separation of aromatic hydrocarbons. The typical gas-chromatograms are shown in Fig. 6. The stratigraphic distributions and diagenetic changes of various organic and inorganic materials of these sediments had been investigated by a joint study on the diagenesis of sedimentary rocks.[23] These sediments were reported to contain extractable organic compounds (EOC), which increased with the depth, but decreased notably in the bottom of this sequence, as shown in Fig. 7a together with the amounts of the total organic carbon (TOC).[25] The estimated concentrations of the phenanthrenes at the 12 sediment horizons over the stratigraphic sequence are plotted in Fig. 7b. Hydrocarbons included in the EOC in the lower part of the sequence formed petroleum in the Shinjo oil field.[25] Several widely accepted maturity parameters, such as vitrinite reflectance and Rock–Eval T_{max}, of these sediments increased with the depth of sediment burial.[23,26—28] The stratigraphic distribution of the total amounts of phenanthrenes is in accordance with those of TOC and EOC as well as the other organic compounds already reported, such as *n*-alkanes and

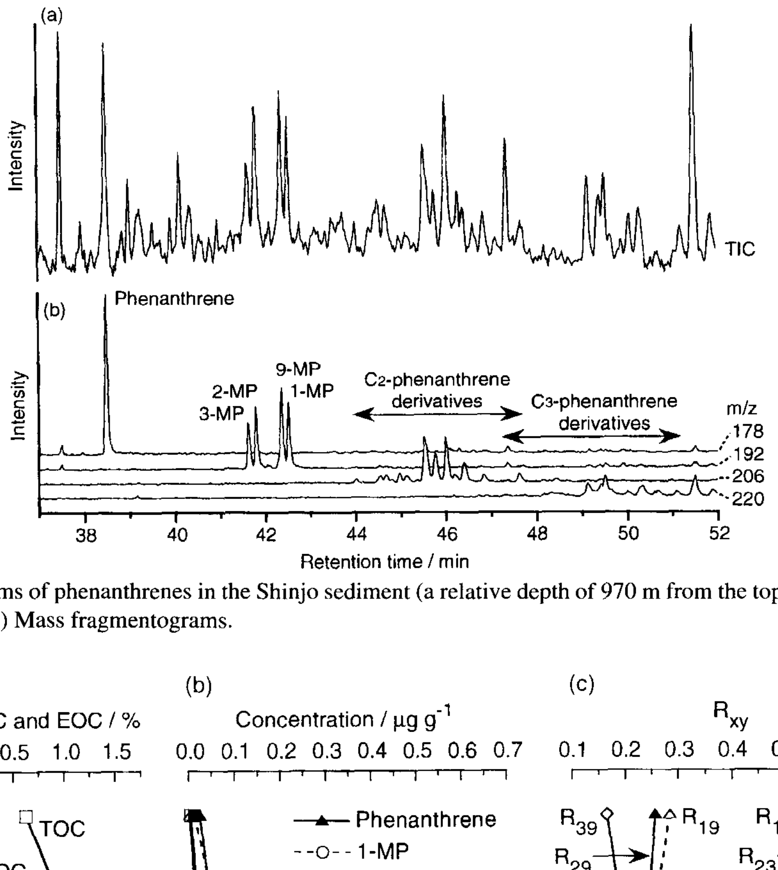

Fig. 6. Gas chromatograms of phenanthrenes in the Shinjo sediment (a relative depth of 970 m from the top sediment). (a) Total ion chromatogram (TIC). (b) Mass fragmentograms.

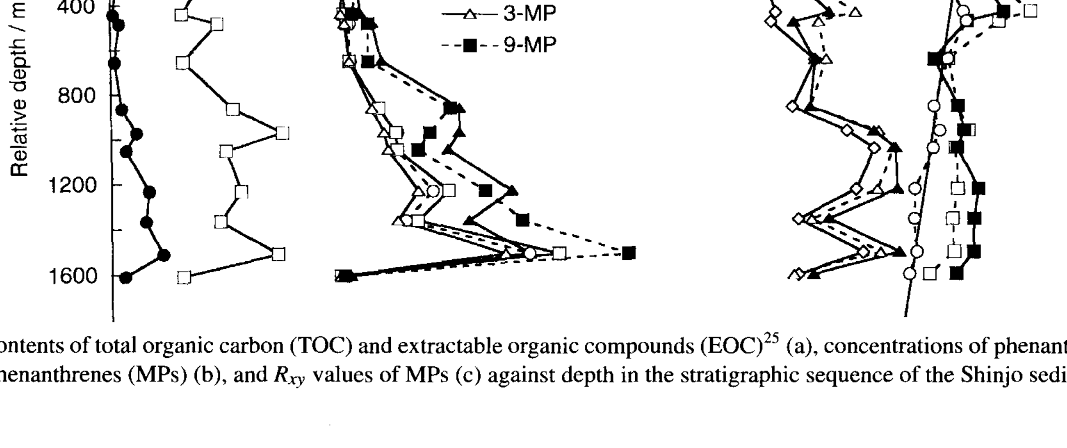

Fig. 7. Contents of total organic carbon (TOC) and extractable organic compounds (EOC)[25] (a), concentrations of phenanthrene and methylphenanthrenes (MPs) (b), and R_{xy} values of MPs (c) against depth in the stratigraphic sequence of the Shinjo sediments.

n-fatty acids.[23] The higher concentrations of 9-MP than those of the other MPs may suggest a rather immature feature of these sediments.

In order to assess the maturity of phenanthrenes in the sediments analyzed, the R_{xy} values were plotted against the sample depth, as depicted in Fig. 7c. There seems to exist three sets of distribution patterns of the R_{xy} value. All R_{x9} values fluctuate greatly, particularly in the lower part of the sequence. The R_{x3} values tend to fluctuate to some extent in the upper part of the sequence, but are practically constant in the lower part. The R_{12} value, on the whole, shows an almost linear relationship with the sediment depth, and changes from 0.54 at the top to 0.45 at the bottom sediment, indicating a decrease in the molar composition of the less stable 1-MP with increasing depth. Since the maturity of the sediments studied here increases with the burial depth, as stated above, the ratio, R_{12}, can be a good parameter for the thermal maturity of phenanthrenes. The new parameter requires the determination of only two isomers of MPs in sediments and, consequently, provides a useful additional indicator for a maturity assessment of sedimentary organic matter.

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