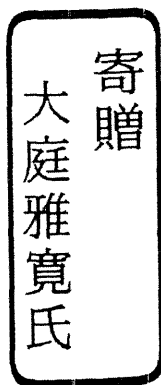# Geochemical Studies on Kerogen Diagenesis

by Thermal Analysis

Masahiro OBA

A dissertation submitted to the Doctoral Program in Chemistry,
the University of Tsukuba in partial fulfillment of the
requirements for the degree of Doctor of Philosophy in Science

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Chapter 1

General Introduction

Since the finding of porphyrin derivatives in crude oils, bitumens and sedimentary rock extracts by Treibs (1936), it has become apparent that the understandings between organic compounds found in the biosphere and lithosphere provide important information on depositional environments, burial history, etc., and furthermore, on the origin of life (Calvin, 1969). More recently, work in organic geochemistry has been stimulated by an interest in the processes involved in the generation of liquid hydrocarbons in the earth's crust and by the development of methods suitable for the evaluation of hydrocarbon deposits. Many of the earlier work concentrated on the analysis of organic molecules with a relatively low molecular weight, which are found in petroleum and the bitumens extracted from oil shales, petroleum source rocks, etc. However, it emerged that a great deal of information would be available to the geochemist if suitable methods could be applied for the analysis of the insoluble fractions of organic matter.

The insoluble fraction of sedimentary organic matter may be classified into humic substance, which is insoluble in organic solvents but are soluble (in part) in alkaline solution, and kerogen, which is insoluble in common organic solvents, alkaline solution, and nonoxidizing acids such as HCl and HF (Forsman and Hunt, 1958; Durand, 1980). The etymological meaning of kerogen is "generating wax" (the Greek *keros* mean wax). The word was coined by A. Crum-Brown (Stewart, 1916) to name the organic matter of the oil shale of the Lothians (Scotland), which produces a waxy oil after pyrolysis.

Kerogen is the most abundant form of organic carbon on earth. It has been estimated that kerogen amounts about 1×10^{22} g compared to about 1×10^{19} g of coal, which itself may be regarded as a mixture of particular types of kerogen, and about 1×10^{18} g of oil (Hunt, 1972; Hunt, 1979). This figure represents 10-15% of the total carbon (organic and inorganic) contained in the earth's crust (Table 1-1).

Table 1-1. Quantities of the different forms of carbon in the earth's crust.

Forms of carbon	Quantities g
Kerogen	1×10^{22}
Carbonates	
in sedimentary rocks	6×10^{22}
in non sedimentary rocks	1×10^{22}
dissolved in oceans	5×10^{19}
Elemental carbon (mainly in basaltic, granitic and metamorphic rocks)	1×10^{22}
Dissolved in oceans (CO_2, organics)	1×10^{18}
Atmosphere (CO_2)	1×10^{18}
Biomass (living organisms)	$0.3 \sim 3 \times 10^{18}$

(from Hunt, 1972)

Kerogen originates in organic debris that has been reworked by organisms living at the water-sediment interface. When depth of burial increases, the proportion of kerogen in the organic matter decreases as hydrocarbons and other soluble or volatile molecules are progressively formed. This is mainly a result of the thermal decomposition of kerogen as the temperature increases (kerogen diagenesis). Therefore, it has been widely accepted that petroleum hydrocarbons are generated mainly from kerogen during diagenesis.

The thermal decomposition of kerogen upon burial proceeds through a multitude of chemical reactions that are unknown in detail (Philippi, 1965; Welte, 1965) but which are recognized to be quasi-irreversible (Huck and Karweil, 1955; Hanbaba and Jüntgen, 1969; Tissot, 1969). Although petroleum generation results from a million-year long process, the process is not in thermodynamic equilibrium in the subsurface. Indeed, such an equilibrium would result mostly in dry gas and polyaromatic carbon residue (Dayhoff *et al.*, 1967; Takach *et al.*, 1987). Consequently, the generation of petroleum in nature is controlled by chemical reaction kinetics, in particular by non-isothermal kinetics, because temperature changes as a function of time under geological conditions (Tissot and Espitalié, 1975). Appropriate kinetic models for the thermal decomposition of kerogen with a consideration of geothermal histories, both individually optimized to the source rock of interest, should therefore, be a promising tool for calculating the timing and intensity of hydrocarbon generation and enhance the efficiency of petroleum exploration.

In view of the complexity of the chemical reaction kinetics for petroleum generation from kerogen, caused by numerous parallel and successive reactions, "macrokinetic" or gross kinetic concepts were developed to simplify the problem of modeling these processes for geological purposes. Based on early work of van Krevelen

et al. (1951), Pitt (1962) and German coal scientists on non-isothermal reaction kinetics (Jüntgen, 1964; Hanbaba, 1967; Jüntgen and van Heek, 1970), gross petroleum generation curves obtained by laboratory heating experiment are approximated by the linear combination of a number of first-order kinetic equations, each of these being characterized by an activation energy and the pre-exponential (frequency) factor. To date, two types of parallel reaction models exist, depending on the spectrum of activation energies be continuous or discrete. Continuous models assume commonly a Gaussian distribution which has the advantage of reducing the number of free parameters to determine (Braun and Burnham, 1987). Discrete models use generally a spacing of 1 or 2 kcal/mol between consecutive activation energies, resulting in ten to twenty parameters to optimize (Tissot and Espitalié, 1975). Activation energies and pre-exponential factors for thermal decomposition of kerogen are determined by these kinetic models using data obtained by laboratory heating experiments of kerogen.

For many years, Rock-Eval pyrolysis method (Ungerer *et al.*, 1986; Tissot *et al.*, 1987; Burnham *et al.*, 1987; Ungerer and Pelet, 1987; Sweeney *et al.*, 1990; Jarvie, 1991) and the programmed micropyrolysis method (Burnham and Braun, 1990; Braun *et al.*, 1991) have been used widely for determination of kinetic parameters. These pyrolysis methods give three peaks by detection, which correspond to those for hydrocarbons (peak S_1) in free form, hydrocarbons (peak S_2) released from kerogen, and CO_2 (peak S_3) from kerogen during heating with temperature increasing programming. The determination of kinetic parameters is based on the T_{max} (temperature at peak top) and shape of peak S_2 captured from at least three Rock-Eval pyrolysis runs performed using different heating rates. Since the peak S_2 include mixtures of compounds, their activation energies and pre-exponential factors are only average values of the mixtures. Each compound on the release from kerogen has its own

values of activation energy and pre-exponential factor. However, it is impossible to determine these values for each compound by these methods. It is better to know precise activation energies and pre-exponential factors of individual compounds not only for academic studies, but also for the petroleum exploration.

The purpose of this study

In the present study, the author performed geochemical study on kerogen diagenesis by thermal analysis based on a reaction kinetic model, and attempted to determine an activation energy and pre-exponential factor for individual compounds on release from kerogen and release extents of those compounds in a sedimentary sequence. The author used kerogen samples prepared from Neogene sediments collected at outcrops along the Oashizawa route in the Shinjo basin in Yamagata Prefecture, Northeastern Japan (Taguchi *et al.*, 1983). The joint study on the organic and inorganic diagenesis in this sequence revealed that petroleum formation took place mainly in the Kusanagi Formation (Taguchi *et al.*, 1986).

A three-step approach was taken to achieve the objectives.

In Chapter 2, the author used a thermogravimetric analyzer (TG) with a gas chromatograph-mass spectrometer (GC/MS) or a mass spectrometer (MS) in order to identify compounds from kerogen as many as possible and reveal the changes of composition and release-temperatures of compounds with increasing burial depth.

In Chapter 3, the author analyzed kerogens by TG-GC/MS and TG-MS methods to obtain the activation energy and pre-exponential factor for an individual compound on release from kerogen. Here the author reports the results of thermal investigation of kerogen and the determination of the values of the activation energy and pre-exponential factor for individual compounds.

In Chapter 4, the author used a mathematical model to know release extents of individual compounds from kerogen, using parameters such as activation energy and pre-exponential factor for reaction kinetics and temperature and rate of subsidence for thermal history of sediments. Here the author reports the results of the application of the model to the stratigraphic sequence of the Neogene Shinjo sediments and compare the results to the depth profiles of solvent extractable hydrocarbons reported for the sediments.

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Chapter 2

Investigation of Organic Compounds Released from Kerogen

in Neogene Sediments of the Shinjo Basin, Japan

by a Laboratory Heating Experiment

ABSTRACT - Kerogens in sediments of different burial depth over a stratigraphic sequence in the Neogene Shinjo sedimentary basin were heated from room temperature to 800 °C under a helium flow by a thermogravimetric analyzer (TG). Compounds released by the thermal decomposition of kerogen were introduced into and analyzed by a gas chromatograph-mass spectrometer (GC/MS). Two hundred and forty-nine compounds were identified and are mainly aliphatic and aromatic hydrocarbons. A release profile of each compound from kerogen with increasing heating temperature was obtained by TG-MS. In general, thermal release of compounds started around 350 °C which shifted to 450 °C with increasing burial depth of kerogen and ended roughly at 550°C. The release-peak width became narrower with increasing burial depth of kerogen, which reflects the loss of a thermally more labile fraction of kerogen in sediments during diagenesis.

INTRODUCTION

Kerogen accounts for a major portion of sedimentary organic matter and its thermal analysis is important to the study of organic diagenesis and petroleum formation. In other words, there remain many problems on the formation of hydrocarbons from kerogen, one of which is a thermal behavior of kerogen during diagenesis.

Among various analytical methods for the study of kerogen, heating experiment is a useful one which provides information on the release of chemical constituents from kerogen in relation to petroleum formation. In this respect, the Rock-Eval instrument has been developed (Espitalié *et al.*, 1985a and b, and 1986). However, the Rock-Eval analysis gives only three peaks of detections, i.e., peaks for extractable hydrocarbons, thermogenic hydrocarbons from kerogen, and CO_2 from kerogen. Komiya *et al.* (1990) combined a thermogravimetric analyzer (TG) with a gas chromatograph-mass spectrometer (GC/MS) or a mass spectrometer (MS). This combined instrument enabled to identify individual compounds thermally released from kerogen, as well as to estimate release temperatures of compounds from kerogen.

In this chapter, the author applied TG-GC/MS and TG-MS to kerogens from the Neogene Shinjo sediments in order to identify compounds as many as possible and reveal the changes of composition and release-temperatures of compounds from kerogen with increasing burial depth.

SAMPLES

Kerogen samples used in this heating experiments were prepared from the Neogene sediment samples collected from outcrops along the River Oashizawa in the Shinjo basin in Yamagata Prefecture, northeastern Japan, in 1980, as common samples for the study of organic and inorganic constituents and their diagenesis (Taguchi *et al.*, 1983). The sediment samples are mainly marine shales and mudstones from Middle Miocene to Pliocene, and were numbered discontinuously from No. 90105 (bottom) to No. 83110 (top) of the 1600 m thick sedimentary sequence (Fig. 2-1). Some results of the joint study were summarized by Taguchi *et al.* (1986).

The method for preparation of kerogen was reported in the study of stable carbon isotopic ratios of kerogen (Shimoyama and Matsubaya, 1985). The author used portions of then-prepared eleven kerogen sample Nos. 83110, 83109, 83108, 83107, 83106, 83105, 83103, 83101, 90101, 90102 and 90104 in this study.
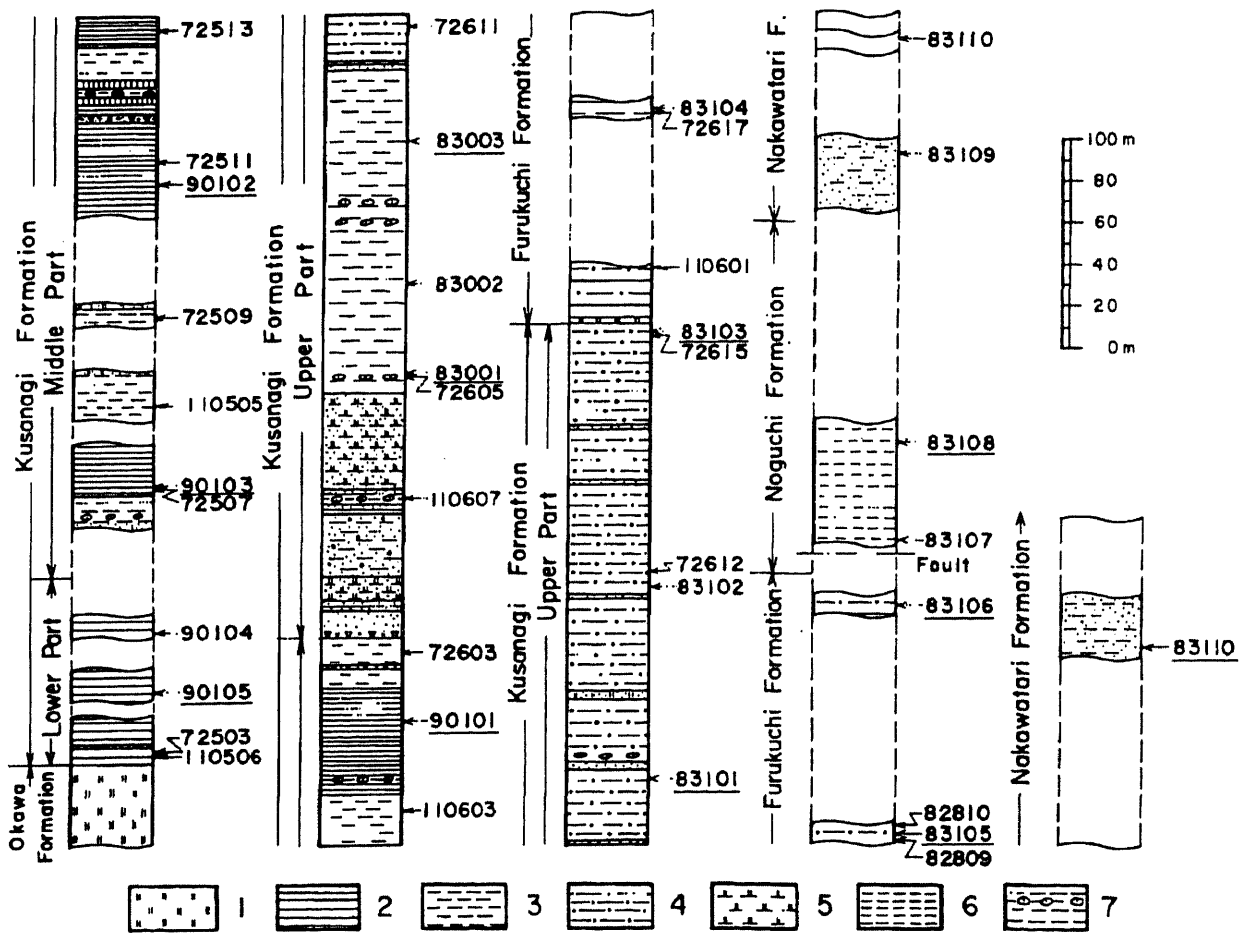
Fig. 2-1. Schematic stratigraphic and lithologic sections of the studied area.

Major rock facies: 1: Dark brown andestic tuff breccia; 2: Very hard siliceous shale; 3: Grey hard siltstone; 4: Dark grey hard siltstone; 5: Sandy tuff; 6: Grey sandy siltstone; 7: Calcareous concretion. (Taguchi *et al.*, 1986)

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EXPERIMENTS

The instrument configuration was reported by Komiya *et al.* (1990). The kerogen sample was heated under a helium flow from room temperature to 800°C at a rate of 60 °C min^{-1} in the TG (Shimadzu TGA-50). During heating experiment, the TG constantly stored data of kerogen weight loss.

In the TG-GC/MS method, compounds released from kerogen by the heating experiment were transported by the helium flow and stored in a cold trap in liquid nitrogen. The trap was made of an uncoated fused silica capillary tube (1m x 0.25 mm i.d.). After the heating experiment, the trap was placed in the GC oven preheated at 30 °C. The temperature of the oven was increased according to the temperature-increasing program mentioned later. The trapped compounds were vaporized in the trap by the temperature increase and introduced to the GC/MS (GC: Hewlett Packard 6890, MS: Hewlett Packard 5973 Mass Selective Detector) by the helium flow. A capillary column used for GC separation was a DB-5HT (30 m x 0.25 mm i.d., J&W Scientific). The GC oven temperature was programmed from 30 to 40°C at a rate of 1 °C min^{-1}, from 40 to 60°C at 2°C min^{-1}, from 60 to 100°C at 3°C min^{-1}, from 100 to 200°C at 4°C min^{-1} and from 200 to 350°C at 5°C min^{-1}. The MS was scanned every 0.31 sec over *m/z* 40 - 500 in an electron impact mode at 70 eV. The data obtained were stored in the computer with a library search system of NIST (the National Institute of Standards and Technology, USA, 1992). The compounds were identified by comparison of peak retention times (or their relative retention times) on mass fragmentograms and their mass spectra with those of standard compounds or mass spectra of NIST data. The relative retention times used were from literature (Larter *et al.*, 1979; Alexander *et al.*,

1983; Rowland *et al.*, 1984; Hartgers, 1992; Ioppolo *et al.*, 1992; George *et al.*, 1998).

In the TG-MS method, released compounds were introduced directly and immediately to MS by the helium flow. The MS was scanned every 0.31 sec over m/z 40 - 550 in an electron impact mode at 70 eV.

RESULTS AND DISCUSSION

TG analysis

TG result of kerogen sample No. 83101 (carbon content 19.4%) is shown in Fig. 2-2. A small peak (1) around 350 °C and a large one (3) around 600 °C were observed in the differential TG curve, and attributed to the decomposition of poorly crystallized pyrite and ordinary crystallized one, respectively, present in the kerogen sample. A broad peak (2) over 400-550 °C is quite likely due to kerogen decomposition. The weight loss of the bulk kerogen sample was 41.6%, and that of kerogen itself was 11.9% based on the TG curve. The other kerogen samples showed nearly similar patterns of TG curve to that of the sample No. 83101. The weight losses due to thermal decomposition of kerogen were also about 10% in the other kerogen samples.

TG-GC/MS analysis

Figure 2-3 shows a total ion chromatogram of compounds released from kerogen sample No.83105. A total of 249 peaks was identified, and compound names corresponding to the peaks are listed in Table 2-1. The 62 compounds with a filled circle were identified by retention times and mass spectra of standard compounds. They are mainly aliphatic and aromatic hydrocarbons, and phenolic compounds. The 77 compounds with an open circle were identified by doublet peak distribution patterns for n-alkane and n-alk-1-ene homologues, and by peak distribution patterns for C_2-C_4 alkylbenzene and C_2 and C_3 alkylnaphthalene isomers. The homologues and isomers were also identified by mass fragmentograms obtained from mass spectra in literature (Larter et $al.$, 1979; Alexander et $al.$, 1983; Rowland et $al.$, 1984; Hartgers, 1992;
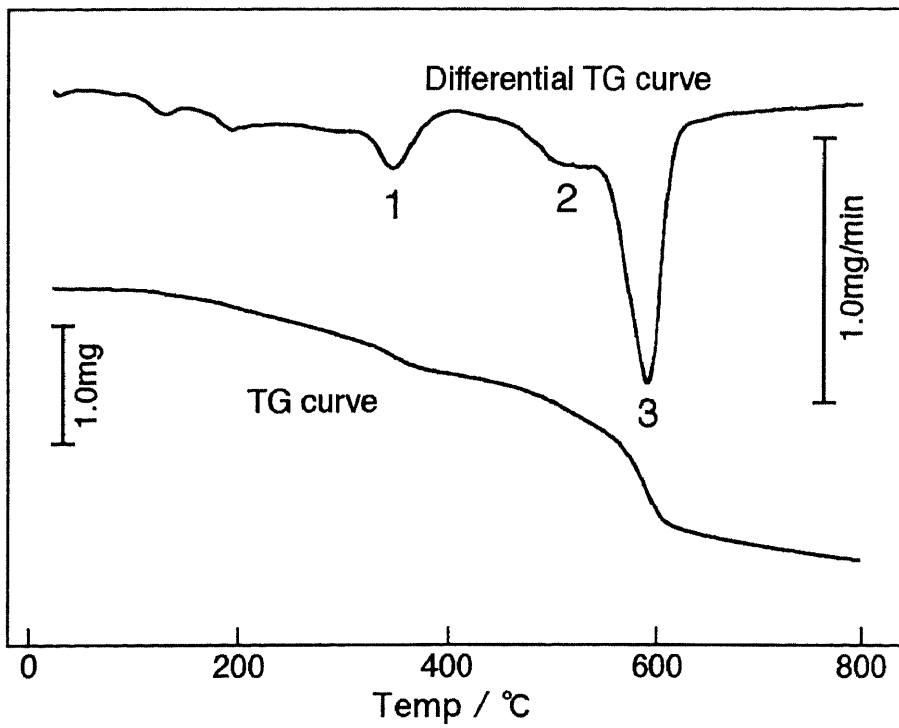
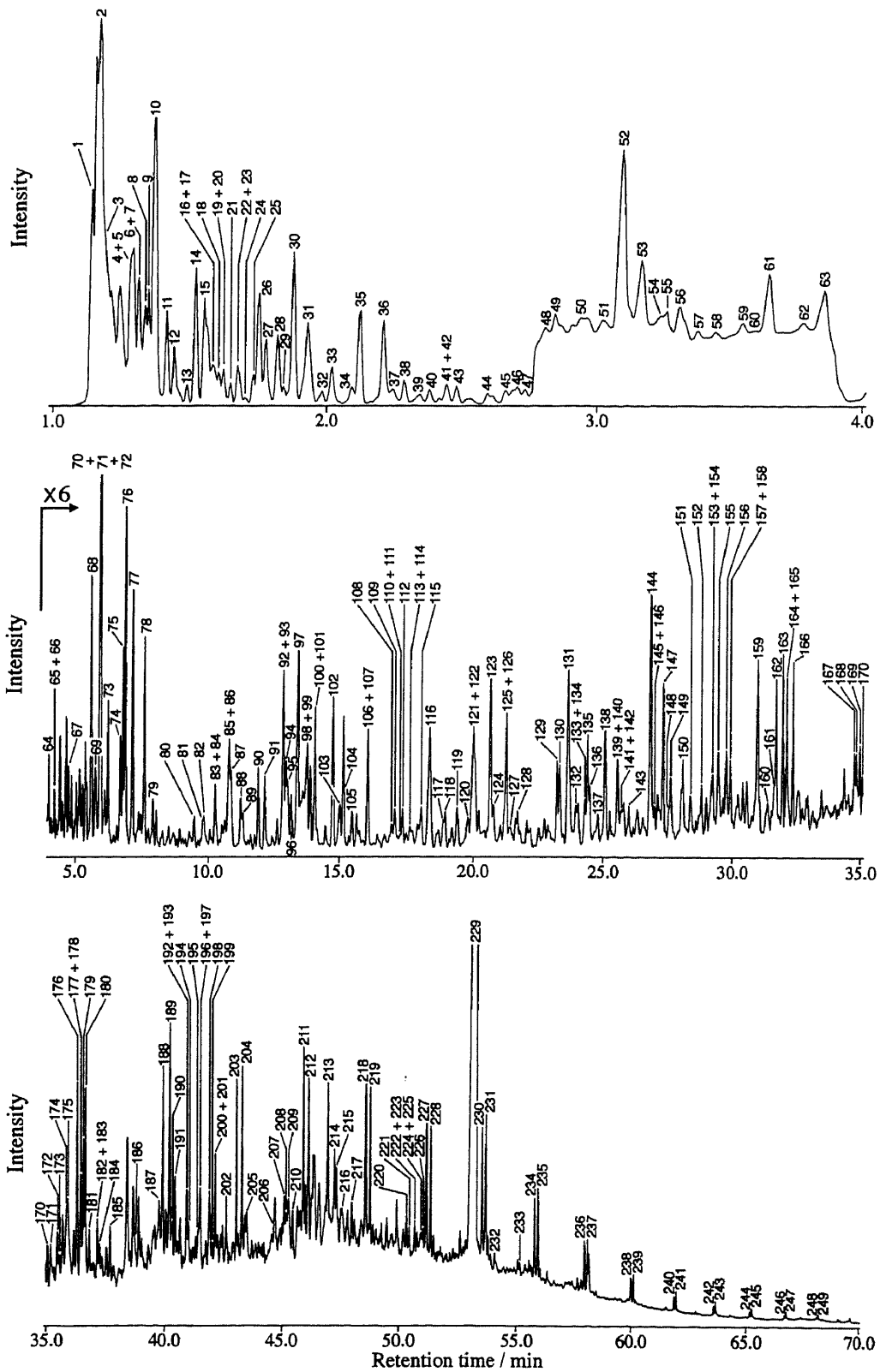Fig. 2-2. Thermogravimetric analysis of kerogen sample No. 83101.

Fig. 2-3. Total ion chromatogram of compounds released from kerogen sample No. 83105.

Table 2-1. Compounds released from kerogen sample No. 83105.

No.	Compounds	No.	Compounds
1	Carbon dioxide	64	C_8H_{16}
2	Sulfur dioxide	65	C_8H_{16}
3	C_4H_8	66	C_8H_{18}
4	C_5H_{10}	67	C_9H_{18}
5	C_5H_{12}	68	O Ethylbenzene
6	C_5H_8	69	C_2-alkylthiophene
7	C_5H_{10}	70	O m- Xylene
8	C_5H_{10}	71	O p- Xylene
9	C_5H_8	72	C_2-alkylthiophene
10	Carbon disulfide	73	C_2-alkylthiophene
11	C_6H_{12}	74	C_2-alkylthiophene
12	C_6H_{14}	75	Styrene
13	C_6H_{14}	76	O o- Xylene
14	O Hex-1-ene	77	O Non-1-ene
15	O Hexane	78	O Nonane
16	C_6H_{12}	79	C_9H_{18}
17	C_6H_{12}	80	$C_{10}H_{22}$
18	C_6H_{10}	81	C_9H_{10}
19	C_6H_{10}	82	$C_{10}H_{22}$
20	C_6H_{12}	83	O n- Propylbenzene
21	C_6H_{12}	84	n- Propylthiophene
22	C_6H_{10}	85	● 1-Ethyl-3-methylbenzene
23	C_6H_{12}	86	C_3-alkylthiophene
24	C_6H_{12}	87	● 1-Ethyl-4-methylbenzene
25	C_6H_{10}	88	● 1,3,5-Trimethylbenzene
26	C_6H_8	89	C_3-alkylthiophene
27	C_6H_8	90	● 1-Ethyl-2-methylbenzene
28	C_6H_{10}	91	C_3-alkylthiophene
29	C_6H_{10}	92	O 1,2,4-Trimethylbenzene
30	Benzene	93	● Benzofuran
31	Thiophene	94	C_9H_{10}
32	C_7H_{16}	95	C_9H_{10}
33	C_6H_{12} (Cyclohexane ?)	96	C_9H_{10}
34	C_7H_{14}	97	O Dec-1-ene
35	O Hept-1-ene	98	● Phenol
36	O Heptane	99	● Isobutylbenzene
37	C_7H_{12}	100	O Decane
38	C_7H_{14}	101	● sec.- Butylbenzene
39	C_7H_{12}	102	● 1,2,3-Trimethylbenzene
40	C_7H_{14}	103	● 1-Methyl-3-isopropylbenzene
41	C_7H_{12}	104	● 1-Methyl-4-isopropylbenzene
42	C_7H_{14}	105	C_9H_{10}
43	C_7H_{12}	106	Indene
44	C_7H_{14}	107	● 1-Methyl-2-isopropylbenzene
45	C_7H_{12}	108	O 1,3-Diethylbenzene
46	C_7H_{10}	109	O 1-Methyl-3-propylbenzene
47	C_7H_{10}	110	● 1,4-Diethylbenzene
48	C_7H_{10}	111	O 1-Methyl-4-propylbenzene
49	C_7H_{10}	112	● n- Butylbenzene
50	C_7H_{12}	113	● 1,2-Diethylbenzene
51	C_7H_{10}	114	O 1,3-Dimethyl-5-ethylbenzene
52	Toluene	115	O 1-Methyl-2-propylbenzene
53	Methylthiophene	116	● o- Cresol
54	C_7H_{10}	117	O 1,4-Dimethyl-2-ethylbenzene
55	Acetic acid	118	O 1,3-Dimethyl-4-ethylbenzene
56	Methylthiophene	119	O 1,2-Dimethyl-4-ethylbenzene
57	C_8H_{16}	120	O 1,3-Dimethyl-2-ethylbenzene
58	C_8H_{16}	121	● m- Cresol
59	C_8H_{16}	122	O p- Cresol
60	C_8H_{16}	123	O Undec-1-ene
61	O Oct-1-ene	124	O 1,2-Dimethyl-3-ethylbenzene
62	C_8H_{14}	125	● Undecane
63	● Octane	126	● 2,6-Dimethylphenol

● Compounds identified by retention times and mass spectra of standards.
O Compounds identified by distribution patterns for homologues and isomers.

Table 2-1. (*continued*).

No.	Compounds	No.	Compounds
127	● 1,2,4,5-Tetramethylbenzene	190	○ 1,3,7-Trimethylnaphthalene
128	● 1,2,3,5-Tetramethylbenzene	191	○ 1,3,6-Trimethylnaphthalene
129	$C_{10}H_{10}$	192	○ 1,3,5-Trimethylnaphthalene
130	$C_{10}H_{10}$	193	○ 1,4,6-Trimethylnaphthalene
131	○ 1,2,3,4-Tetramethylbenzene	194	○ 2,3,6-Trimethylnaphthalene
132	● 2-Ethylphenol	195	○ 1,2,6-Trimethylnaphthalene
133	○ *n*- Pentylbenzene	196	○ 1,2,7-Trimethylnaphthalene
134	C5-alkylbenzene	197	○ 1,6,7-Trimethylnaphthalene
135	● 2,4-Dimethylphenol	198	● Fluorene
136	● 2,5-Dimethylphenol	199	○ 1,2,4-Trimethylnaphthalene
137	$C_{11}H_{16}$	200	○ 1,2,5-Trimethylnaphthalene
138	● Naphthalene	201	○ *n*- Nonylbenzene
139	● 4-Ethylphenol	202	○ 1,2,3-Trimethylnaphthalene
140	Benzothiophene	203	● Hexadec-1-ene
141	● 3,5-Dimethylphenol	204	○ Hexadecane
142	○ 3-Ethylphenol	205	Methyldibenzofuran
143	● 2,3-Dimethylphenol	206	Alkylazulene
144	● Dodec-1-ene	207	Alkylazulene
145	● 3,4-Dimethylphenol	208	○ *n*- Decylbenzene
146	C3-alkylphenol	209	Methylfluorene
147	○ Dodecane	210	Methylfluorene
148	C5-alkylbenzene	211	○ Heptadec-1-ene
149	$C_{12}H_{24}$	212	○ Heptadecane
150	$C_{13}H_{28}$	213	○ Prist-1-ene
151	C3-alkylphenol	214	○ Prist-2-ene
152	C3-alkylphenol	215	● Phenanthrene
153	$C_{11}H_{12}$	216	● Anthracene
154	C3-alkylphenol	217	○ *n*- Undecylbenzene
155	$C_{11}H_{12}$	218	● Octadec-1-ene
156	$C_{11}H_{12}$	219	○ Octadecane
157	$C_{11}H_{12}$	220	● 3-Methylphenanthrene
158	○ *n*- Hexylbenzene	221	● 2-Methylphenanthrene
159	● 2-Methylnaphthalene	222	○ 2-Methylanthracene
160	Methylbenzothiophene	223	○ *n*- Dodecylbenzene
161	Methylbenzothiophene	224	● 9-Methylphenanthrene
162	● 1-Methylnaphthalene	225	○ 1-Methylanthracene
163	○ Tridec-1-ene	226	● 1-Methylphenanthrene
164	$C_{14}H_{28}$	227	○ Nonadec-1-ene
165	$C_{10}H_{14}O$	228	● Nonadecane
166	○ Tridecane	229	S8
167	○ *n*- Heptylbenzene	230	● Eicos-1-ene
168	$C_{12}H_{14}$	231	○ Eicosane
169	$C_{12}H_{10}$ (Biphenyl ?)	232	● Fluoranthene
170	$C_{12}H_{14}$	233	● Pyrene
171	C2-alkylbenzothiophene	234	○ Heneicos-1-ene
172	○ 2-Ethylnaphthalene	235	○ Heneicosane
173	○ 1-Ethylnaphthalene	236	○ Docos-1-ene
174	● 2,6-Dimethylnaphthalene	237	● Docosane
175	● 2,7-Dimethylnaphthalene	238	○ Tricos-1-ene
176	● Tetradec-1-ene	239	○ Tricosane
177	● 1,3-Dimethylnaphthalene	240	○ Tetracos-1-ene
178	● 1,7-Dimethylnaphthalene	241	○ Tetracosane
179	● 1,6-Dimethylnaphthalene	242	○ Pentacos-1-ene
180	● Tetradecane	243	● Pentacosane
181	$C_{12}H_{10}$	244	○ Hexacos-1-ene
182	● 1,4-Dimethylnaphthalene	245	○ Hexacosane
183	● 2,3-Dimethylnaphthalene	246	○ Heptacos-1-ene
184	● 1,5-Dimethylnaphthalene	247	○ Heptacosane
185	● 1,2-Dimethylnaphthalene	248	○ Octacos-1-ene
186	○ *n*- Octylbenzene	249	● Octacosane
187	● Dibenzofuran		
188	○ Pentadec-1-ene		
189	● Pentadecane		

Ioppolo *et al.*, 1992; George *et al.*, 1998). The 110 compounds without a circle were identified by comparison with mass spectra of NIST data.

The major released compounds are aliphatic hydrocarbons, as indicated by the homologous series of *n*-alkanes and *n*-alk-1-enes ranging from C_6 to C_{28}, C_2 - C_4 alkylbenzenes, and polycyclic aromatic hydrocarbons and their alkyl derivatives in all samples. These compounds are known to be present as main compounds in petroleum, supporting that petroleum hydrocarbons were generated from kerogen in the sediments. Branched alkenes (prist-1-ene and prist-2-ene), phenol, alkyl phenols, thiophenes, and alkyl thiophenes were also found in relatively high abundance.

Table 2-2 shows relative abundance of aliphatic and aromatic hydrocarbons, and phenolic compounds released from the 11 kerogen samples which are listed from top to bottom according to their relative depth in the sedimentary sequence. The released amounts of aliphatic hydrocarbons increase gradually with increasing depth. However, those of higher molecular aliphatic hydrocarbons, i.e., eicosane and eicos-1-ene, decrease drastically at the depth of kerogen sample Nos. 90102 and 90104. Activation energies of higher molecular aliphatic hydrocarbons in thermal decomposition of kerogen are smaller than those of lower molecular ones (Tang and Stauffer, 1994; Tang and Béhar, 1995; Béhar *et al.*, 1997). Therefore, the absence of the higher molecular aliphatic hydrocarbons in kerogen sample Nos. 90102 and 90104 is probably due to their earlier release from kerogen during diagenesis before the kerogen reached at those depths.

The released amount of 1,3,5-trimethylbenzene increases with increasing kerogen depth, whereas that of 1,2,3-trimethylbenzene is higher in the kerogen samples at upper and middle depth than at bottom three samples. The different profiles may indicate that those compounds had come from different precursors and/or followed different reaction

Table 2-2. Compounds released from the eleven kerogen samples.

Kerogen	Decane	Dec-1-ene	Pentadecane	Pentadec-1-ene
83110	-	-	-	-
83109	+	++	+	+
83108	+	++	+	+
83107	+	++	+	+
83106	+	++	+	+
83105	++	++	+	++
83103	++	++	++	++
83101	++	+++	++	++
90101	++	+++	++	++
90102	++	++	++	++
90104	++	++	++	++

Kerogen	Eicosane	Eicos-1-ene	1,3,5-Trimethylbenzene	1,2,3-Trimethylbenzene
83110	-	·	-	+
83109	-	-	+	+++
83108	+	+	+	+++
83107	+	+	+	+++
83106	-	-	+	+++
83105	+	+	+	+++
83103	+	+	+	+++
83101	+	+	++	+++
90101	++	++	++	++
90102	-	-	++	++
90104	-	-	++	++

Kerogen	Naphthalene	1,6-Dimethylnaphthalene .	Phenanthrene	Phenol
83110	-	-	-	++
83109	-	-	-	++++
83108	+	-	-	+++
83107	-	-	-	+++
83106	+	+	-	+++
83105	+	+	-	+++
83103	+	+	+	+++
83101	+	+	+	++
90101	+	-	-	++
90102	-	-	-	++
90104	+	-	-	++

Symbols, ++++, +++, ++, +, -, and · indicate very much major, very major, major, moderate, minor, and trace amounts of compounds released from kerogen samples.

pathways during diagenesis. The relatively high abundance of 1,2,3-trimethylbenzene likely indicates that precursors derived from non-aromatic carotenoids (e.g., β , β - carotene) had incorporated into kerogen and they yielded 1,2,3-trimethylbenzene during the heating experiment (Hartgers *et al.*, 1994).

The highly released amounts of polycyclic aromatic hydrocarbons (e.g. naphthalene, 1,6-dimethylnaphthalene and phenanthrene) from kerogen samples around the middle depth were observed. The depth profiles of the polycyclic aromatic and aliphatic hydrocarbons are similar to those of extractable polycyclic aromatic and aliphatic hydrocarbons, respectively (Shioya and Ishiwatari, 1983) in the sediments. This similarity suggests that the hydrocarbons in the sediments were mainly generated from kerogen during diagenesis.

Phenol was released in abundance from kerogen sample No. 83109 specially, and shows a gradually decrease with increasing kerogen depth. The depth profiles of most C_1 and C_2 alkylphenols show similar patterns to that of phenol, although the data are not shown in the text. It is generally accepted that phenolic compounds have been derived from lignin components incorporated into kerogen. In the study of stable carbon isotopes, it is reported that the source of organic matter changed from marine to terrestrial toward the upper part of the sedimentary sequence (Shimoyama and Matsubaya, 1985). Therefore, it is likely that the depth profile of phenol abundance mainly reflects the change of depositional environment, although a possibility that the profile is partly affected by diagenesis can not be excluded.

TG-MS analysis

Figures 2-4 to 2-8 show continuous release profiles (along temperature) of compounds from kerogen sample Nos. 83109, 83105, 83101, 90101 and 90104. These

Fig. 2-4. Thermal release patterns of five selected ions corresponding to the compounds shown by the ions from kerogen sample No. 83109. A peak intensity shows a relative intensity at the peak maximum.

Fig. 2-5. Thermal release patterns of five selected ions corresponding
to the compounds shown by the ions from kerogen sample No. 83105.
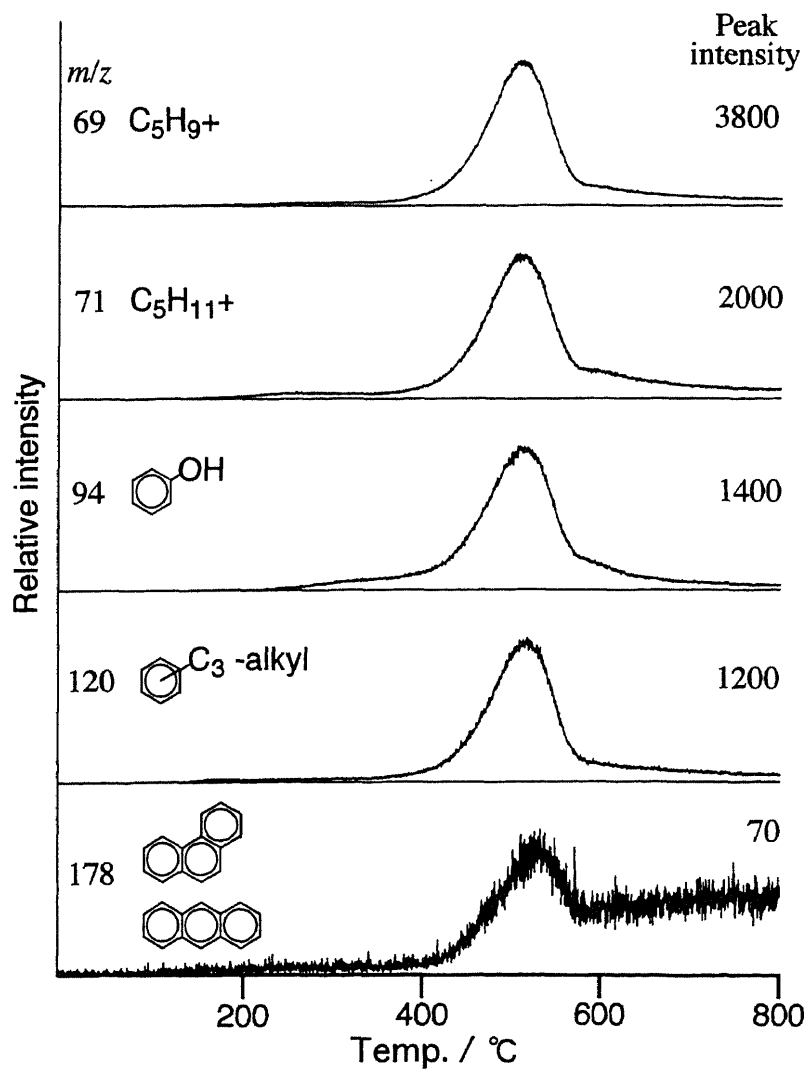
Fig. 2-6. Thermal release patterns of five selected ions corresponding to the compounds shown by the ions from kerogen sample No. 83101.
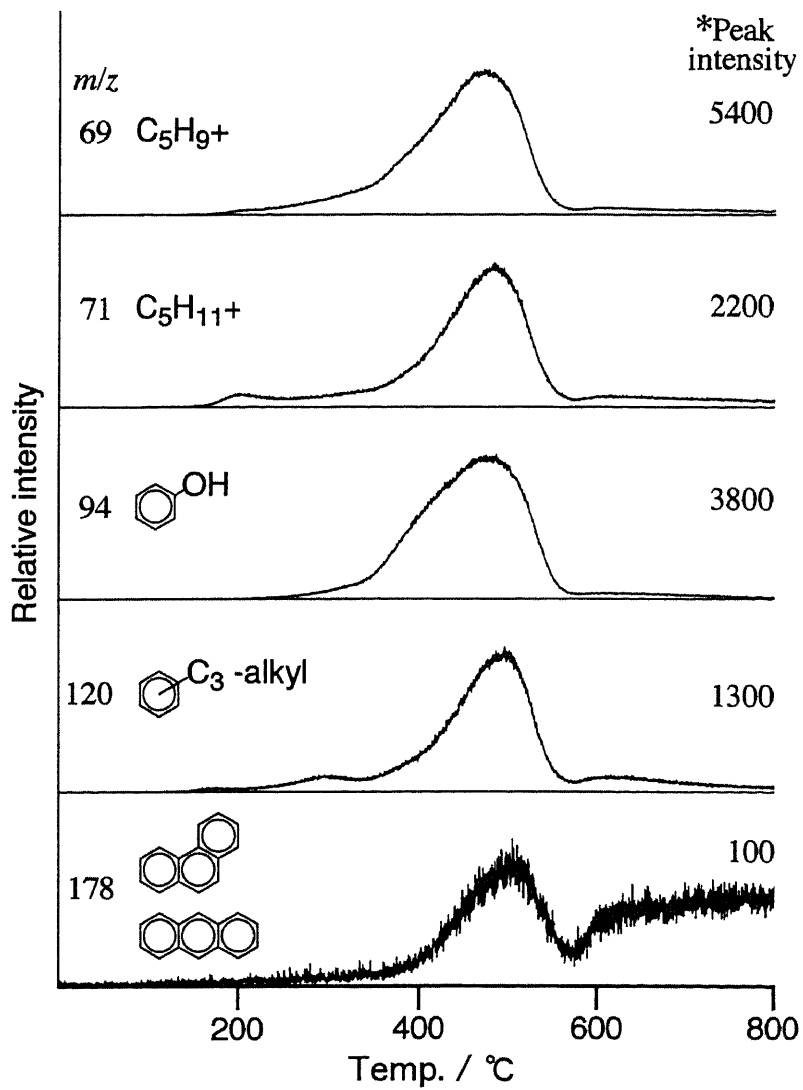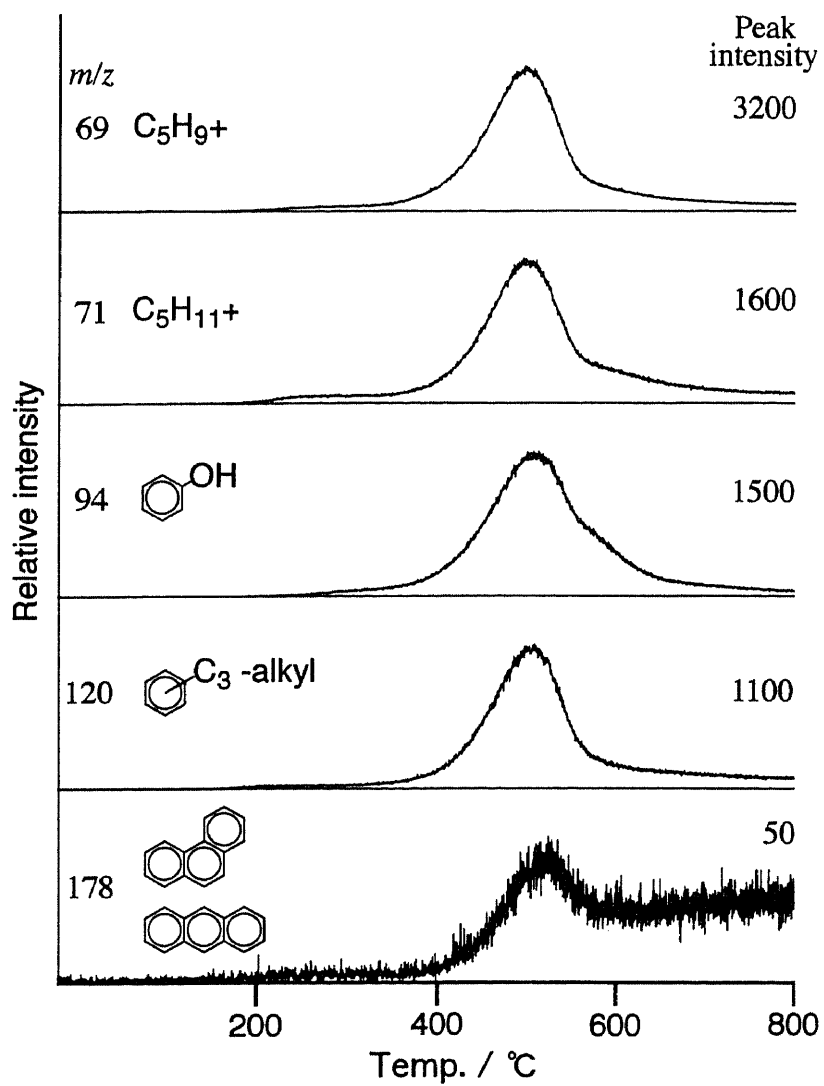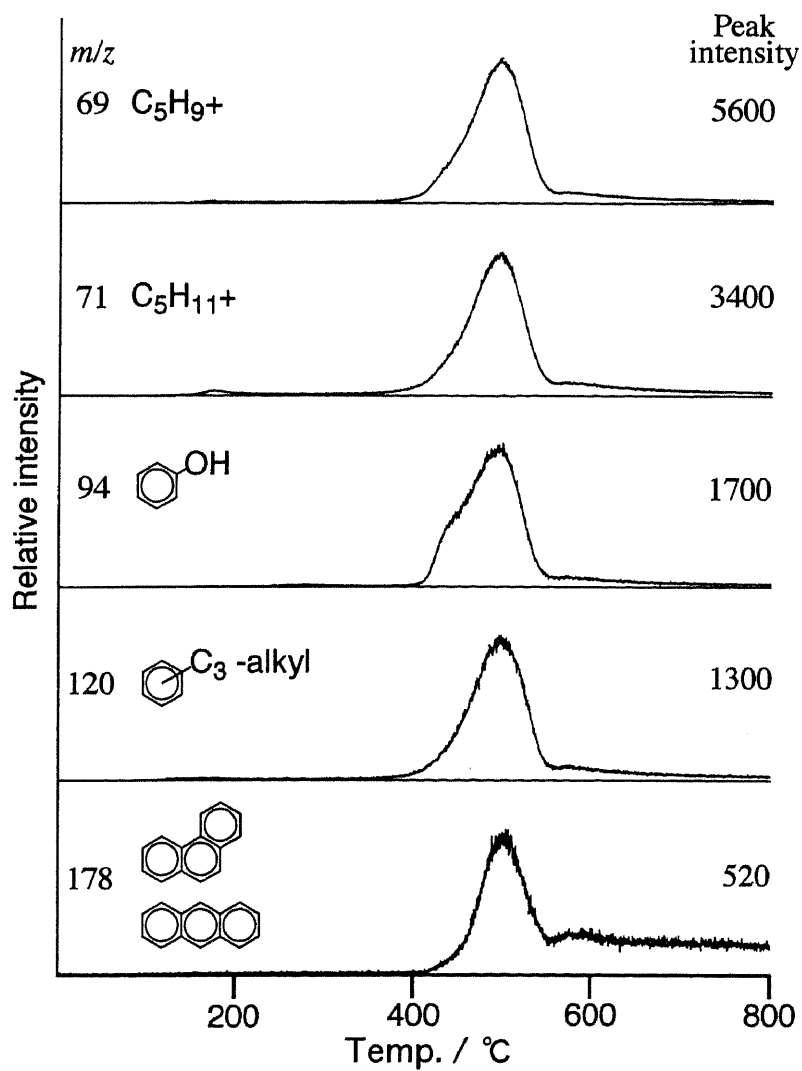
Fig. 2-7. Thermal release patterns of five selected ions corresponding to the compounds shown by the ions from kerogen sample No. 90101.
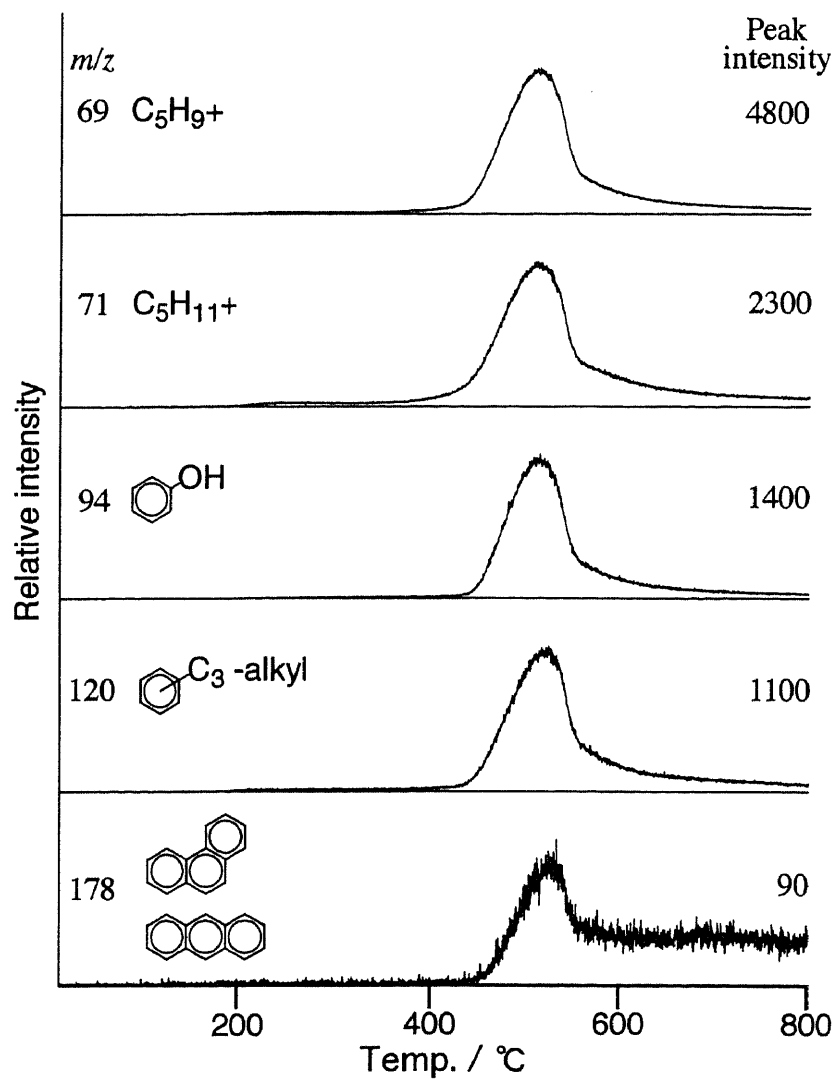
Fig. 2-8. Thermal release patterns of five selected ions corresponding to the compounds shown by the ions from kerogen sample No. 90104.

kerogen samples were chosen over the stratigraphic sequence in relation to petroleum formation, because the depth around the sample No. 83001 corresponds to the beginning of the threshold of petroleum generation (Taguchi *et al.*, 1986). Ions at m/z 69 and 71 are the common mass fragments of *n*-alk-1-enes and *n*-alkanes, respectively. The m/z 94 is assigned to phenol, 120 to C_3-alkylbenzenes, and 178 to triaromatic hydrocarbons.

The release peak of compounds from the kerogen sample No. 83109 at a temperature increasing rate of $60\,^\circ C$ min^{-1} starts at around $350\,^\circ C$ and ends at roughly $550\,^\circ C$ with maximum-release at $480\,^\circ C$ as seen in Fig. 2-4. As the depth of the kerogen sample becomes deeper, the starting and maximum-release temperatures shift toward higher. In the kerogen sample No. 90104, the starting and maximum-release are $450\,^\circ C$ and $510\,^\circ C$, respectively (Fig. 2-8). Furthermore, the peak width becomes narrower with increasing burial depth. Kerogen consists of bonds of various strengths (various activation energies). The peak narrowing (or disappearance of the lower temperature part of peak) is probably due to the breakdown of bonds with lower activation energies and the loss of compounds with those bonds as diagenesis proceeded, and gave an apparent shift of the starting and maximum-release toward higher temperature.

CONCLUSIONS

Kerogens of different burial depth from Neogene Shinjo sediments were heated in the TG from room temperature to 800°C under a helium flow, and released compounds were analyzed by GC/MS or MS. The results of these analyses are summarized as follows:

1. Kerogen samples released various kinds of organic compounds during the heating. Among 249 compounds identified, aliphatic and aromatic hydrocarbons were major compounds. These compounds were also found as major compounds in petroleum. Therefore, the result supports that petroleum hydrocarbons were generated from kerogen during diagenesis in the sediments.

2. Examination of continuous release profiles of individual compounds from kerogen along heating temperature showed that compound releases started at around 350°C and ended at roughly 550°C with maximum-release at 480°C at the upper part of the sequence.

3. As the depth of kerogen becomes deeper, the starting and maximum-release temperatures shifted toward higher, making the release peak narrower. The apparent shift of the temperatures was likely due to the earlier loss of compounds bonding to kerogen with lower activation energies.

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Chapter 3

Determination of Activation Energy and Pre-exponential Factor

for Individual Compounds on Release from Kerogen

by a Laboratory Heating Experiment

ABSTRACT - Kerogen recovered from Neogene Shinjo sediments were heated from room temperature to 800 °C using a thermogravimetric analyzer (TG). Organic compounds released from kerogen during heating were trapped and analyzed by a gas chromatograph (GC)-mass spectrometer (MS). Among these compounds, benzene, hexane, toluene, phenol, heptane and indene were selected to determine temperatures at which maximum release of these compounds occurred based on TG-MS peak profiles. This analysis was carried out using programmed heating rates (Hr) of 5, 10, 20, 30, and 60 °C min^{-1} and five temperatures at peak tops (T_{max} in absolute temperature) were determined for each compound. The plot of $1/T_{max}$ vs ln $(Hr/(T_{max})^2)$ for each compound showed a good straight line with a high correlation coefficiency. Accordingly, a mean activation energy (E_0) and pre-exponential factor (A) at E_0 for each compound on the release from kerogen were calculated, using the equation of the approximate method (or Gaussian E-distribution method) by Braun and Burnham (1987),

$$\ln (Hr/(T_{max})^2) = - E_0/RT_{max} + \ln (AR/E_0)$$

where R is the ideal gas constant. The activation energies and pre-exponential factors of these compounds were in a range of 43.1 to 60.9 kcal/mol and of 3.56 x 10^{10} to 1.21 x 10^{16} s^{-1}, respectively. The averages of the activation energies and pre-exponential factors obtained from the five kerogens had decomposition rates in order of indene > benzene, toluene > phenol > hexane, heptane, which indicated that hexane and heptane were more strongly bound to kerogen than the three aromatic hydrocarbons.

INTRODUCTION

It has been widely accepted that petroleum hydrocarbons are generated mainly by thermal decomposition of kerogen in sediments. Some studies described the hydrocarbon generation from kerogen by kinetic models using data obtained by heating experiments. The Rock-Eval pyrolysis method has been used for that purpose (Ungerer et al., 1986; Tissot et al., 1987; Burnham et al., 1987; Ungerer and Pelet, 1987; Sweeney et al., 1990; Jarvie, 1991). This pyrolysis method gives three peaks by detection, which correspond to those for hydrocarbons in free form, hydrocarbons released from kerogen, and CO_2 from kerogen. Since the first two peaks include mixtures of compounds, their activation energies and pre-exponential (or frequency) factors are only average values of the mixtures. Each compound on the release from kerogen has its own values of activation energy and pre-exponential factor, and therefore it is difficult to determine these values for each compound by this method.

For identification of compounds released from kerogen and for determination of their release temperatures, a thermogravimetric analyzer (TG) was connected to a gas chromatograph-mass spectrometer (GC/MS) and to a mass spectrometer (MS), respectively (Chapter 2). This system enables determination of the activation energy and pre-exponential factor of an individual compound on the release from kerogen by changing the rate of experimental heating on a given sample.

In this chapter, the author examined kerogen in Neogene Shinjo sediments by this approach to obtain the activation energy and pre-exponential factor for an individual compound. The author describes the results of thermal investigation of kerogen and present the values obtained by this technique.

SAMPLES

Kerogen samples used for determination of kinetic parameters are same as described in Chapter 2. Kerogen samples used in this heating experiments were prepared from the Neogene sediment samples collected from outcrops along the River Oashizawa in the Shinjo basin in Yamagata Prefecture, northeastern Japan, in 1980, as common samples for the study of organic and inorganic constituents and their diagenesis (Taguchi *et al.*, 1983). The author used portions of 5 previously prepared kerogen samples Nos. 83109, 83105, 83101, 90101 and 90104 in this study.

EXPERIMENTS

Analytical procedure for TG-GC/MS analysis is same as described in Chapter 2.

In the TG-MS analysis, a kerogen sample was heated in TG under a helium flow from room temperature to 800 °C at increasing rates of 5, 10, 20, 30, and 60 °C min^{-1}. The heating rates were controlled by a thermocouple just above the kerogen sample. Released compounds were introduced directly and without a significant delay to MS by helium flow. MS was scanned every 0.31 sec over m/z 40 - 550 in an electron impact ionization mode at 70 eV.

RESULTS AND DISCUSSION

Identification by TG-GC/MS and TG-MS

Figure 3-1 shows mass fragmentograms of m/z 78, 86, 92, 94, 100, and 116 for the compounds released from the kerogen sample No. 83105 by the TG-GC/MS analysis. The other kerogen samples showed similar mass fragmentograms of those m/z to those of the sample No. 83105.

The mass fragmentogram of m/z 78 by the TG-GC/MS analysis (Fig. 3-1a) showed a large peak at about 1.9 min and a small one at about 1.4 min. These two peaks were identified as benzene and carbon disulfide ($C^{32}S^{34}S$), respectively, based on their mass spectra. The compound release profile of m/z 78 by the TG-MS analysis (Fig. 3-2a) showed a large and a small peak. Because the temperature of the small peak coincided with that of the thermal decomposition of pyrite as revealed by the TG analysis, this peak was carbon disulfide which was probably formed by the reaction of the carbon residue in kerogen and sulfur produced from the thermal decomposition of pyrite in kerogen. Therefore, the large peak on the profiles was assigned to benzene released from kerogen.

The mass fragmentogram of m/z 86 (Fig. 3-1b) showed a large peak at about 1.5 min in retention time and a broad one from about 2.8 to 3.9 min. According to their mass spectra, these two peaks were identified as hexane and tetrafluorosilane (SiF_4), respectively. The m/z 86 corresponds to the molecular ion of hexane and a fragment ion (SiF_3^+) of tetrafluorosilane. The tetrafluorosilane was probably formed during the preparation of kerogen samples. The compound release profile of m/z 86 (Fig. 3-2b) showed two peaks. The peak at about 250 °C was identified as tetrafluorosilane

a) *m/z* 78   Benzene

Peak
intensity

15080

b) *m/z* 86   Hexane

1510

c) *m/z* 92   Toluene

10500

d) *m/z* 94   Phenol

1620

e) *m/z* 100   Heptane

1310

f) *m/z* 116   Indene

1370

Relative intensity

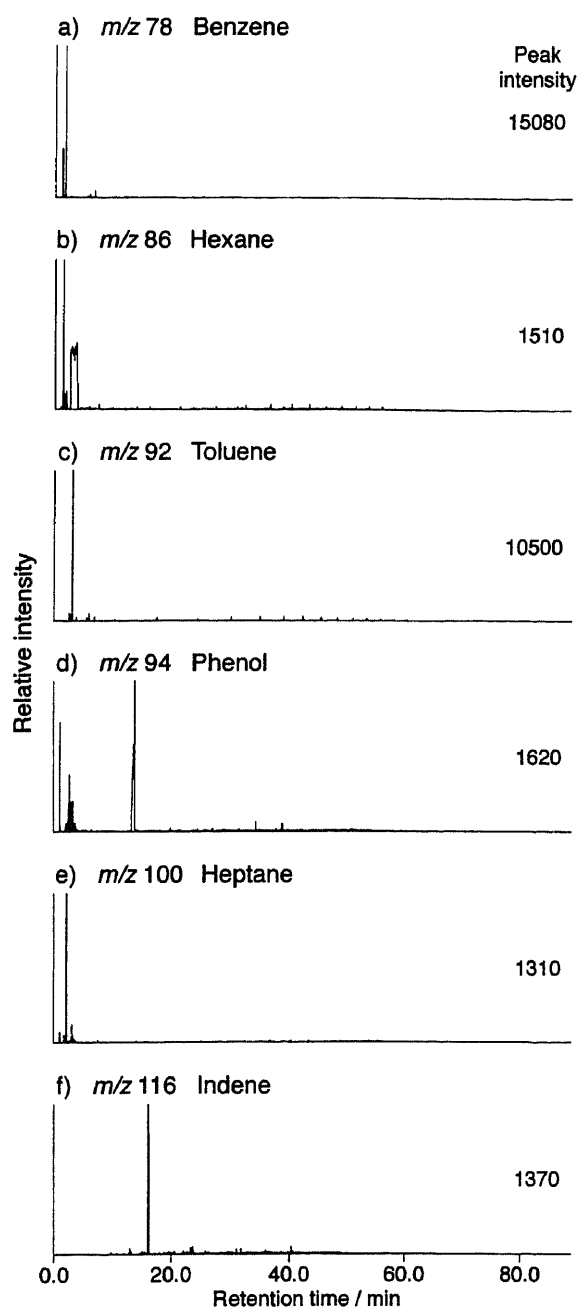0.0   20.0   40.0   60.0   80.0

Retention time / min

Fig. 3-1. Mass fragmentograms (*m/z* 78, 86, 92, 94, 100 and 116) of compounds released from kerogen sample No. 83105 by TG-GC/MS analysis.
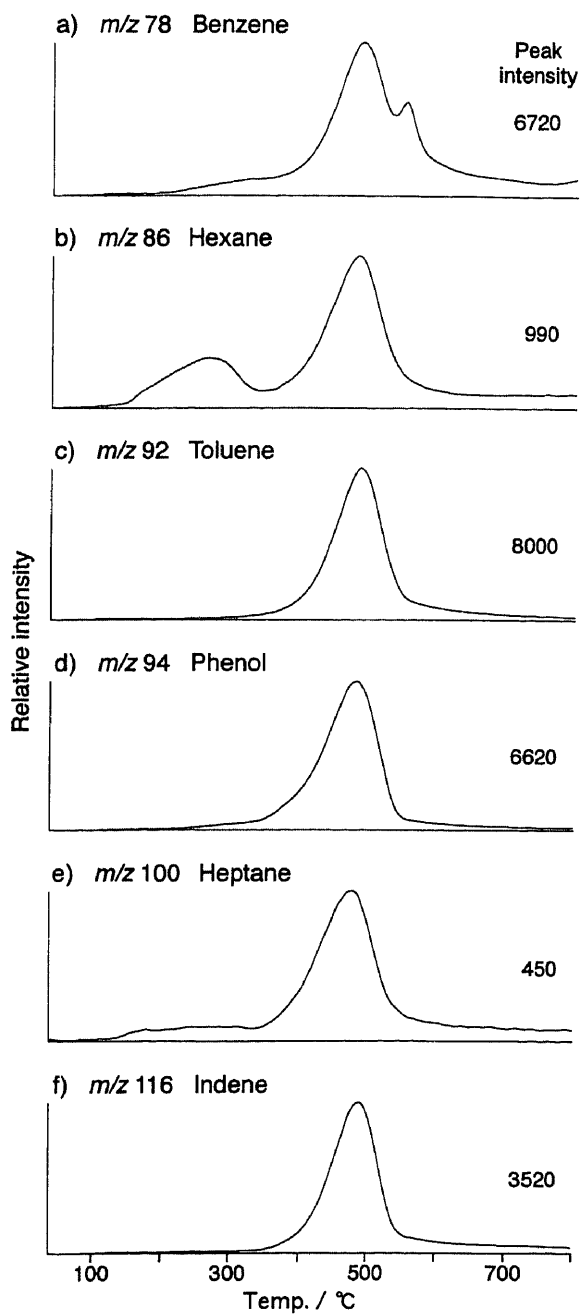
- 43 -

Fig. 3-2. Compound release profiles (*m/z* 78, 86, 92, 94, 100 and 116) from kerogen sample No. 83105 by TG-MS analysis (temperature increasing rate at 20°C min⁻¹).

- 44 -

according to the mass spectrum. Therefore, the peak at about 500 °C was hexane released from kerogen.

The mass fragmentograms of m/z 92, 100 and 116 (Figs. 3-1c, e and f) showed only one peak on the mass fragmentograms. These peaks were assigned to toluene, heptane and indene, respectively, based on their mass spectra. The mass fragmentogram of m/z 94 (Fig. 3-1d) showed one large peak at about 15 min in retention time and some peaks at about 5 min. The large peak was phenol based on retention time, mass spectrum of a standard compound, and its much larger size. Therefore, it was concluded that the peaks on the compound release profiles of m/z 92, 94, 100, and 114 (Figs. 3-2c to f) were of toluene, phenol, heptane and indene, respectively.

On the other mass fragmentograms, more than two peaks were detected. For instance, the mass fragmentograms of m/z 69 (Fig. 3-3a) and 71 (Fig. 3-3b) showed peak distribution patterns of homologous compounds. The ion at m/z 69 corresponds to $C_5H_9^+$ and m/z 71 to $C_5H_{11}^+$, which are common mass fragments of n-alkenes and n-alkanes, respectively. Accordingly, a series of n-alkenes (ranging from C_6 to C_{25}) and a series of n-alkanes (ranging from C_6 to C_{28}) were identified. The mass fragmentograms of m/z 120 (Fig. 3-3c) and 142 (Fig. 3-3d) showed peaks of 7 isomers of C_3-alkylbenzenes (molecular ion 120) and 2 of methylnaphthalenes (molecular ion 142), respectively. Although the compound release profiles of these four mass fragmentograms showed peaks at about 500 °C, each peak consisted of mixtures of above compounds. Therefore, those mass fragmentograms and their compound release profiles were not used for the present purpose.

Determination of T_{max}

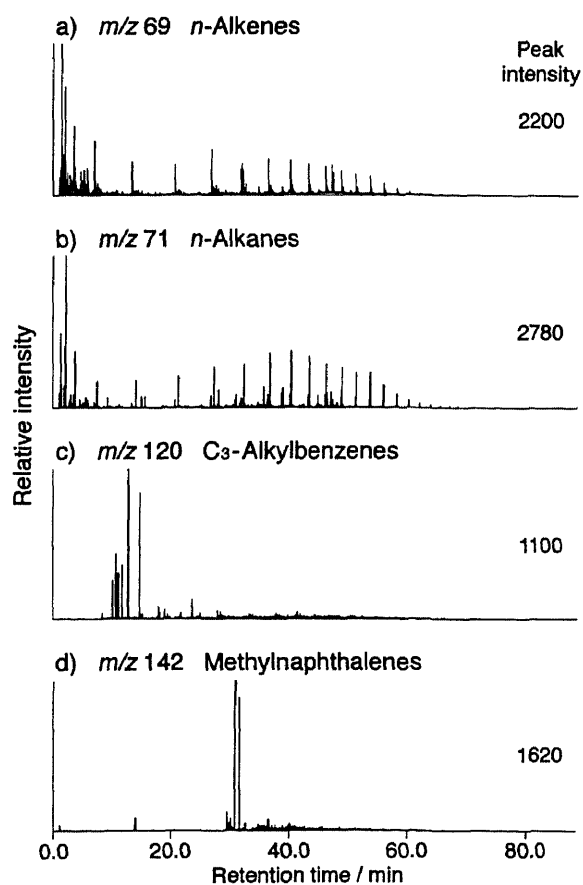Figure 3-4 shows the release profiles of toluene (m/z 92) from the kerogen sample

Fig. 3-3. Mass fragmentograms (m/z 69, 71, 120 and 142) of organic compounds released from kerogen sample No. 83105 by TG-GC/MS analysis.

No. 83105 and Fig. 3-5 of hexane (m/z 100) from No. 90101 heated at temperature

increase rates of 5, 10, 20, 30, and 60 °C min^{-1}. These heating rates were selected for

practical reasons. Considerably lower rates (e.g. 0.1 °C min^{-1}) would require about five

days for the completion of a heating experiment, whereas higher heating rates are

known to cause significant differences between the real temperature of the sample and

the programmed rate. This problem has been discussed in detail by Burnham et al.

(1987).

In order to estimate an activation energy and pre-exponential factor, T_{max}

(temperature at peak top) was determined. For the estimation of the time lag between

compound release from the kerogen sample in TG and detection by MS, the time at the

peak top due to the decomposition of pyrite in the kerogen sample on the differential

TG curve and that of peak top on the compound release profile of m/z 64 for the

molecular ion of SO_2 were compared. Similarly the time lag was determined for each

heating rate. Thus, T_{max} was determined by correcting the observed time at peak top

using the time-temperature graph recorded by TG. Table 3-1 shows T_{max} of benzene,

hexane, toluene, phenol, heptane, and indene at five heating rates. These T_{max} values

shifted toward higher temperatures with increasing heating rates, and fell in a range

between 424.6 and 459.9 °C at 5 °C min^{-1}, and so on as shown in Table 3-1. It is

important to note that a slight change in T_{max} can significantly change the activation

energy and pre-exponential factor. Therefore, considerable care was made to determine

the correct T_{max}.

Activation energy and pre-exponential factor

Assuming a first order reaction for the compound on the release from a kerogen

sample, the activation energy and pre-exponential factor were determined from T_{max}
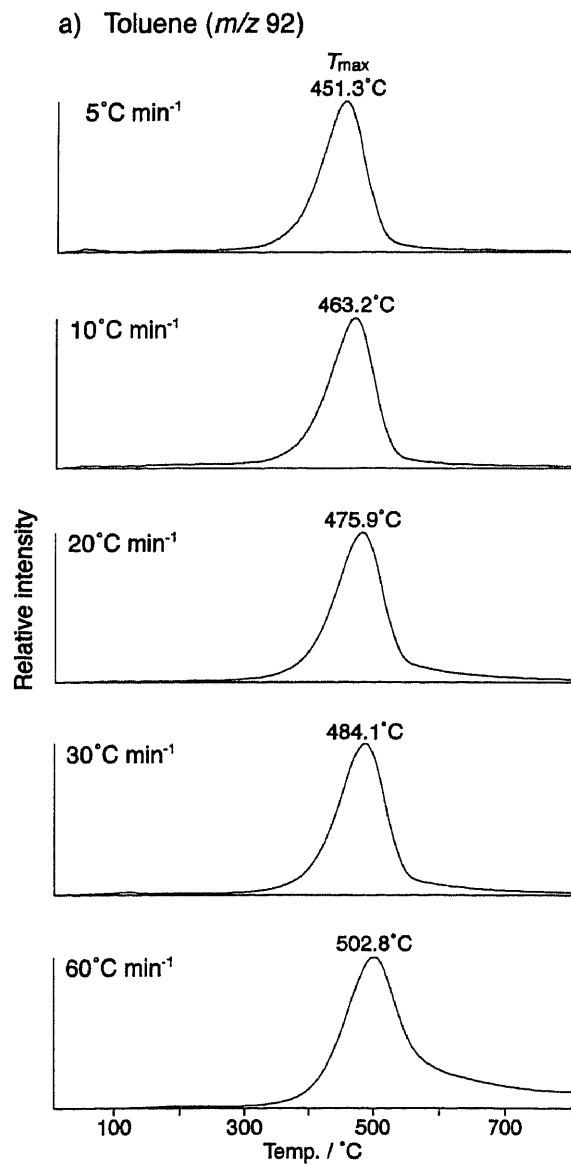
a) Toluene (*m/z* 92)

Fig. 3-4. Compound release profiles of toluene from kerogen sample No. 83105 by TG-MS analysis.

b) Heptane (*m/z* 100)

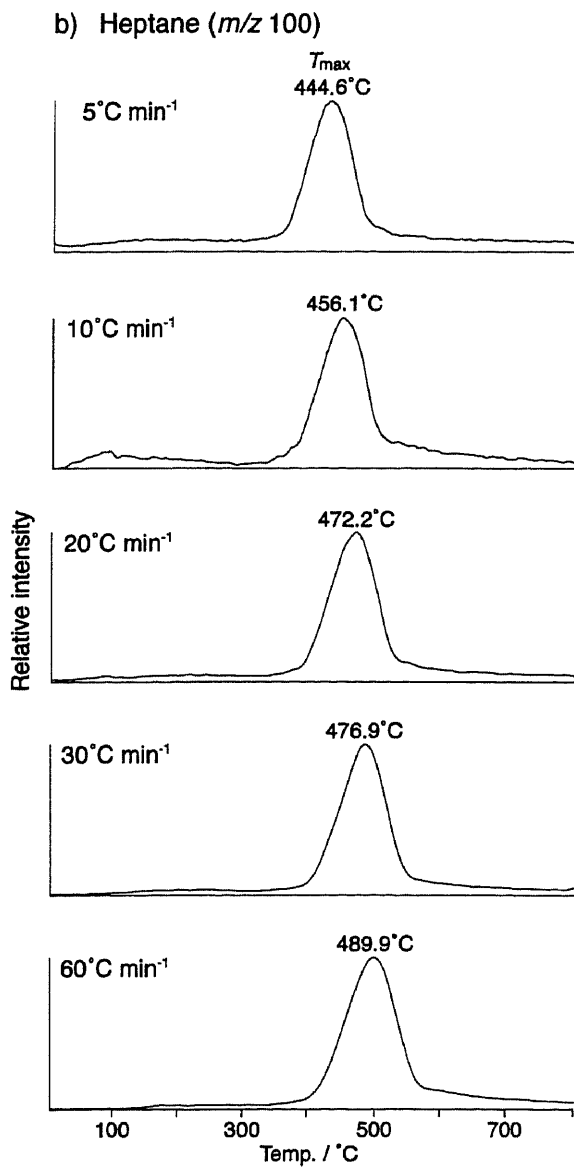

Fig. 3-5. Compound release profiles of heptane from kerogen sample No. 83105 by TG-MS analysis.

Table 3-1. T_{max} of benzene, hexane, toluene, phenol, heptane, and indene on release from kerogen samples in Shinjo sediments.

Kerogen	m/z	Compounds	T_{max} / °C				
			5 °C min^{-1}	10 °C min^{-1}	20 °C min^{-1}	30 °C min^{-1}	60 °C min^{-1}
83109	78	Benzene	439.6	453.7	470.2	477.3	493.4
	86	Hexane	435.6	450.0	460.9	468.1	478.5
	92	Toluene	440.5	455.4	473.4	480.3	494.4
	94	Phenol	428.2	441.0	454.4	461.2	473.8
	100	Heptane	424.6	434.3	449.4	457.6	469.7
	116	Indene	442.1	453.9	473.8	481.3	497.4
83105	78	Benzene	451.2	462.4	475.7	482.5	504.4
	86	Hexane	448.0	458.1	470.1	478.2	494.2
	92	Toluene	451.3	463.2	475.9	484.1	502.8
	94	Phenol	454.8	464.0	476.2	483.7	502.8
	100	Heptane	443.8	455.2	465.0	473.0	488.6
	116	Indene	451.2	464.8	477.9	485.2	510.7
83101	78	Benzene	454.0	466.7	481.6	488.8	511.8
	86	Hexane	452.0	464.5	477.7	485.0	502.5
	92	Toluene	454.0	467.8	481.8	489.1	510.9
	94	Phenol	451.6	464.6	477.4	484.5	504.9
	100	Heptane	447.1	460.4	472.4	481.5	495.9
	116	Indene	452.7	469.1	482.1	489.1	515.7
90101	78	Benzene	453.3	467.2	482.0	487.6	501.9
	86	Hexane	450.1	463.7	477.9	481.9	494.8
	92	Toluene	454.4	467.7	481.1	487.5	499.8
	94	Phenol	449.4	462.1	475.5	480.5	491.9
	100	Heptane	444.6	456.1	472.2	476.9	489.9
	116	Indene	451.4	466.7	480.5	484.6	499.8
90104	78	Benzene	458.1	470.0	479.4	493.6	513.7
	86	Hexane	456.3	465.7	476.3	490.6	506.4
	92	Toluene	459.9	470.8	488.5	494.6	513.7
	94	Phenol	453.6	464.0	478.7	486.2	505.7
	100	Heptane	453.3	464.3	475.8	486.2	501.7
	116	Indene	459.3	470.4	482.3	496.4	516.9

with different heating rates using the equation of the approximate method (or Gaussian E-distribution method) by Braun and Burnham (1987):

$$\ln\,(Hr/(T_{max})^2) = -\,E_0/RT_{max} + \ln\,(AR/E_0)$$

where Hr is the heating rate (K min^{-1}), E_0 the mean activation energy of Gaussian distribution of activation energies, A the pre-exponential factor at E_0, R the ideal gas constant, and T_{max} in K. Figures 3-6 to 3-10 show the plots of $1/T_{max}$ vs. ln $(Hr/(T_{max})^2)$ for benzene, hexane, toluene, phenol, heptane, and indene. All plots showed reasonably straight lines with high correlation coefficiencies (r) from 0.999 (heptane from the kerogen sample No. 83101) to 0.977 (phenol from No. 83105). The activation energies and pre-exponential factors for these compounds on the release from five kerogen samples obtained by these means are listed in Table 3-2. The activation energy and pre-exponential factor of phenol from No. 90101 were 60.9 kcal/mol and 1.21 x 10^{16} s^{-1}, respectively, which was the largest among the values of all released compounds of all kerogen samples. Conversely, 43.1 kcal/mol and 3.56 x 10^{10} s^{-1} for indene from No. 83101 was the lowest. The values of kinetic parameters for each compound did not reflect the difference in kerogens of different burial depth, except that the values for compounds from the kerogen sample No. 90101 were somewhat higher than those for the other kerogen samples.

The rate constants of each compound at 120°C were calculated using the Arrhenius expression (Table 3-2). The joint study on the organic and inorganic diagenesis in the Shinjo sediments concluded that petroleum generation took place mainly in the upper part of the Kusanagi Formation with the onset of the intense generation at 120°C (Taguchi et al., 1986). The fastest and slowest among those values in Table 3-2 were

a) Benzene
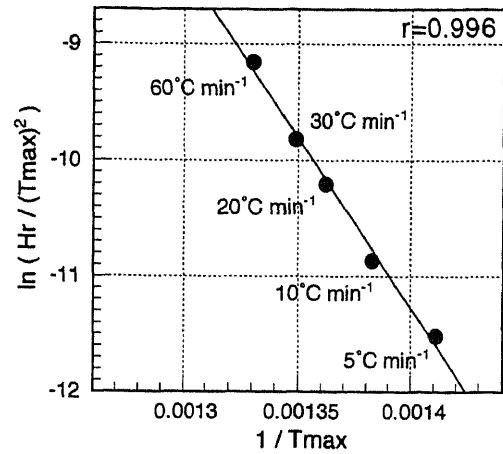
$\ln(\,Hr\,/\,(Tmax)^2\,) = -2.37 \times 10^4\,(1\,/\,Tmax) + 21.7$
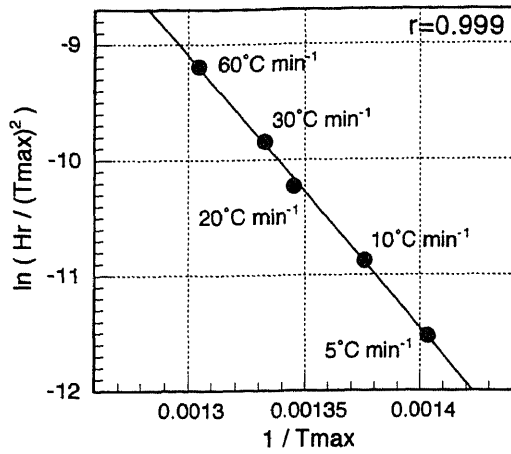
b) Hexane

$\ln(\,Hr\,/\,(Tmax)^2\,) = -2.94 \times 10^4\,(1\,/\,Tmax) + 29.9$

c) Toluene

$\ln(\,Hr\,/\,(Tmax)^2\,) = -2.34 \times 10^4\,(1\,/\,Tmax) + 21.2$
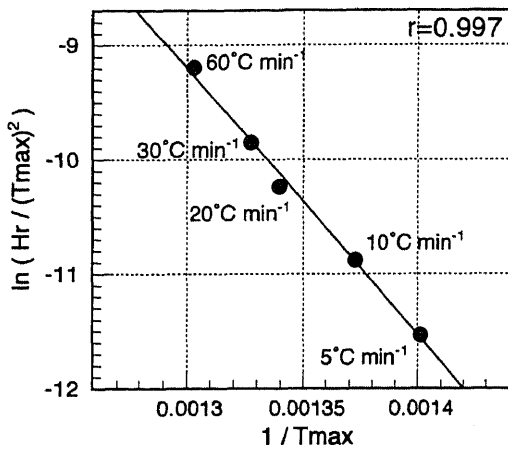
d) Phenol

$\ln(\,Hr\,/\,(Tmax)^2\,) = -2.70 \times 10^4\,(1\,/\,Tmax) + 27.0$

e) Heptane

$\ln(\,Hr\,/\,(Tmax)^2\,) = -2.62 \times 10^4\,(1\,/\,Tmax) + 26.1$

f) Indene

$\ln(\,Hr\,/\,(Tmax)^2\,) = -2.26 \times 10^4\,(1\,/\,Tmax) + 20.1$

Fig. 3-6. $1/\,T_{max}$ - $\ln\,(Hr/(T_{max})^2)$ plots of benzene (a), hexane (b), toluene (c), phenol (d), heptane (e) and indene (f) on the release from kerogen sample No. 83109.

Fig. 3-7. 1/ T_{max} - ln $(Hr/(T_{max})^2)$ plots of benzene (a), hexane (b), toluene (c), phenol (d), heptane (e) and indene (f) on the release from kerogen sample No. 83105.

a) Benzene

$\ln(Hr/(Tmax)^2) = -2.33 \times 10^4 (1/Tmax) + 20.5$

$r=0.993$

60°C min^{-1}
30°C min^{-1}
20°C min^{-1}
10°C min^{-1}
5°C min^{-1}

$\ln(Hr/(Tmax)^2)$
$1/Tmax$

b) Hexane

$\ln(Hr/(Tmax)^2) = -2.65 \times 10^4 (1/Tmax) + 25.0$

$r=0.998$

60°C min^{-1}
30°C min^{-1}
20°C min^{-1}
10°C min^{-1}
5°C min^{-1}

$\ln(Hr/(Tmax)^2)$
$1/Tmax$

c) Toluene

$\ln(Hr/(Tmax)^2) = -2.38 \times 10^4 (1/Tmax) + 21.2$

$r=0.995$

60°C min^{-1}
30°C min^{-1}
20°C min^{-1}
10°C min^{-1}
5°C min^{-1}
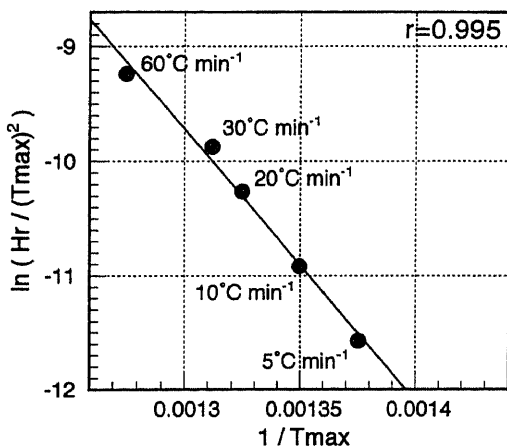
$\ln(Hr/(Tmax)^2)$
$1/Tmax$

d) Phenol

$\ln(Hr/(Tmax)^2) = -2.52 \times 10^4 (1/Tmax) + 23.3$

$r=0.995$

60°C min^{-1}
30°C min^{-1}
20°C min^{-1}
10°C min^{-1}
5°C min^{-1}
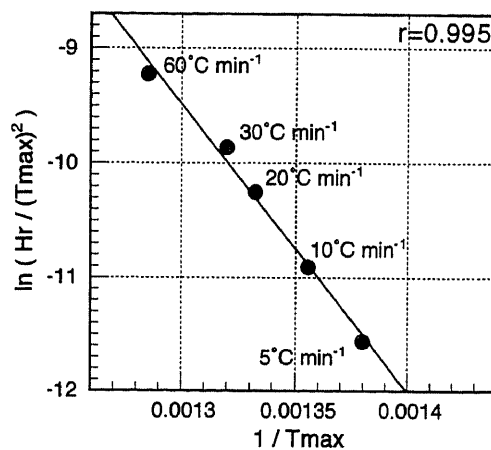
$\ln(Hr/(Tmax)^2)$
$1/Tmax$

e) Heptane

$\ln(Hr/(Tmax)^2) = -2.68 \times 10^4 (1/Tmax) + 25.7$

$r=0.999$

60°C min^{-1}
30°C min^{-1}
20°C min^{-1}
10°C min^{-1}
5°C min^{-1}
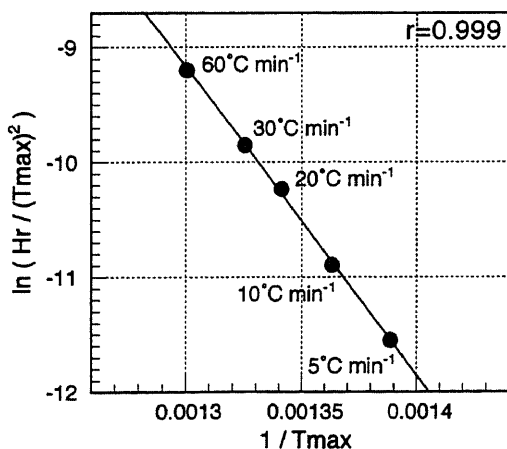
$\ln(Hr/(Tmax)^2)$
$1/Tmax$

f) Indene

$\ln(Hr/(Tmax)^2) = -2.17 \times 10^4 (1/Tmax) + 18.4$

$r=0.988$

60°C min^{-1}
30°C min^{-1}
20°C min^{-1}
10°C min^{-1}
5°C min^{-1}

$\ln(Hr/(Tmax)^2)$
$1/Tmax$

Fig. 3-8. $1/T_{max}$ - $\ln(Hr/(T_{max})^2)$ plots of benzene (a), hexane (b), toluene (c), phenol (d), heptane (e) and indene (f) on the release from kerogen sample No. 83101.

a) Benzene

$\ln (Hr / (Tmax)^2) = -2.74 \times 10^4 (1 / Tmax) + 26.0$
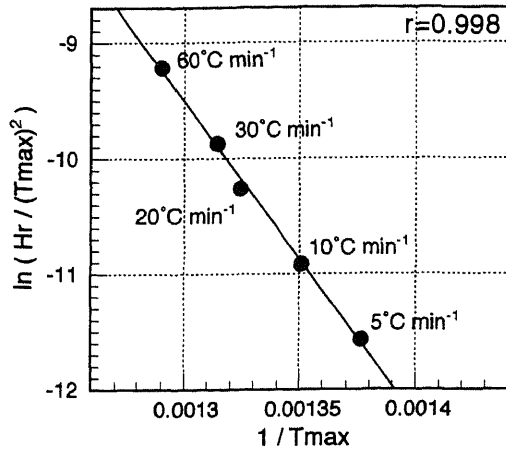
b) Hexane

$\ln (Hr / (Tmax)^2) = -2.94 \times 10^4 (1 / Tmax) + 29.0$
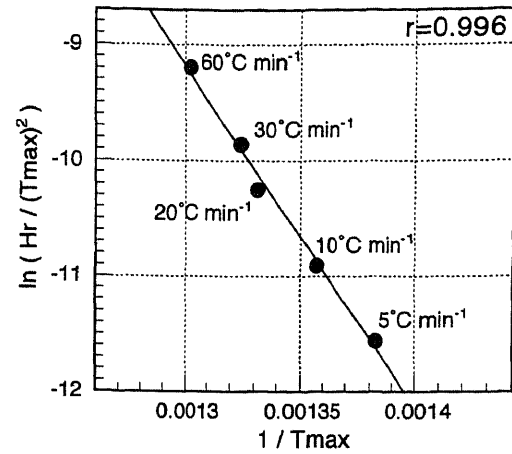
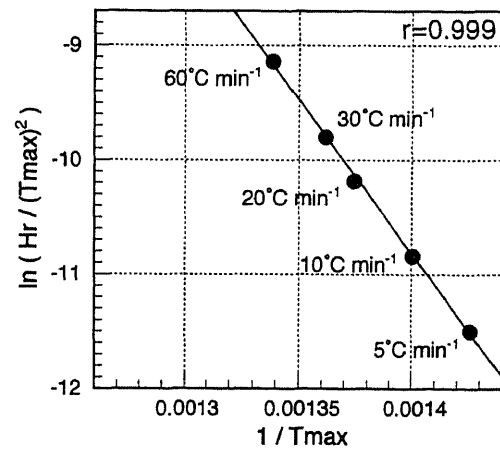c) Toluene

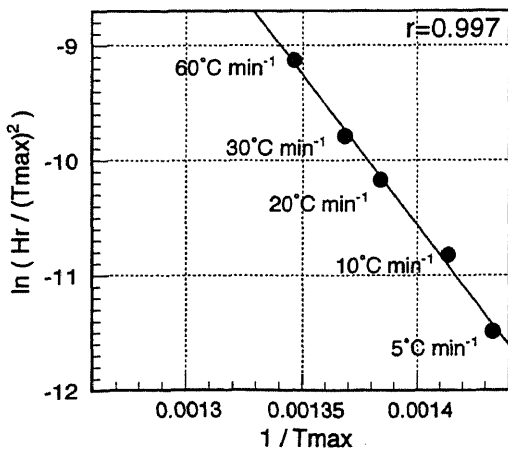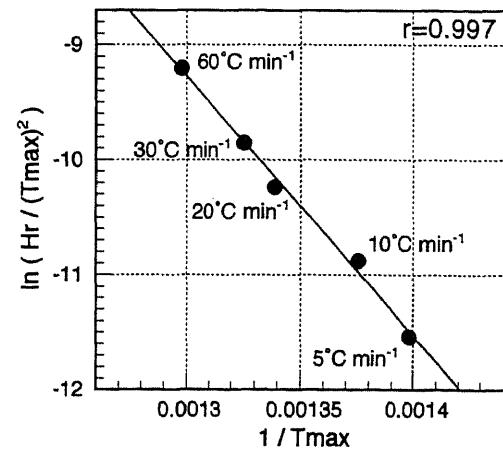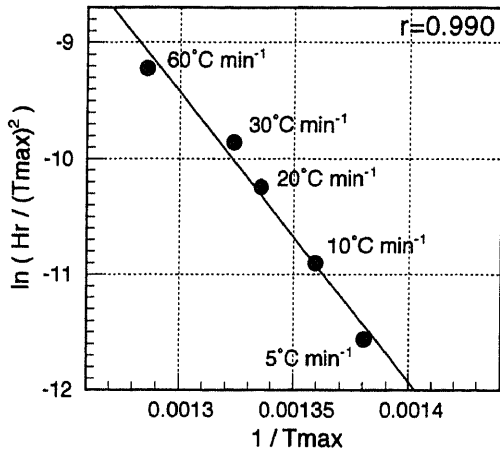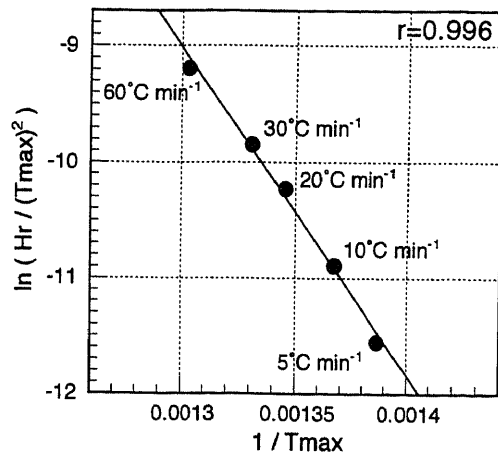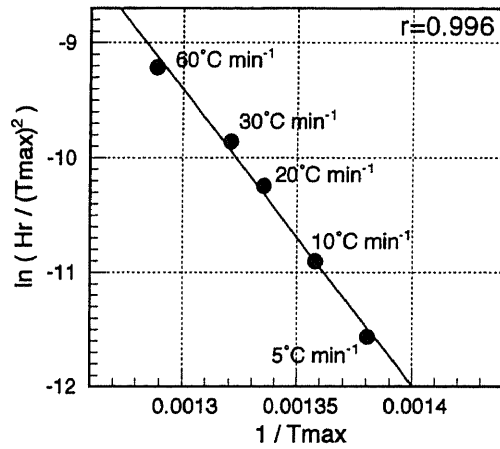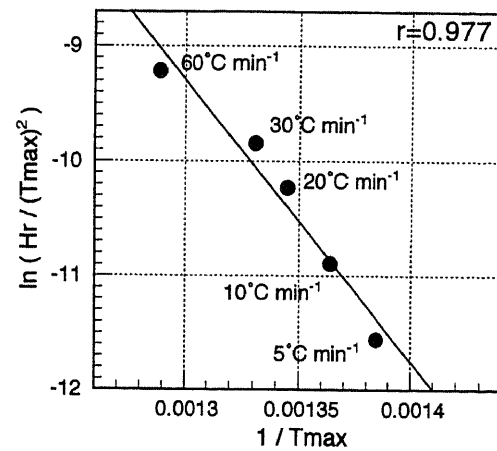$\ln (Hr / (Tmax)^2) = -2.92 \times 10^4 (1 / Tmax) + 28.5$
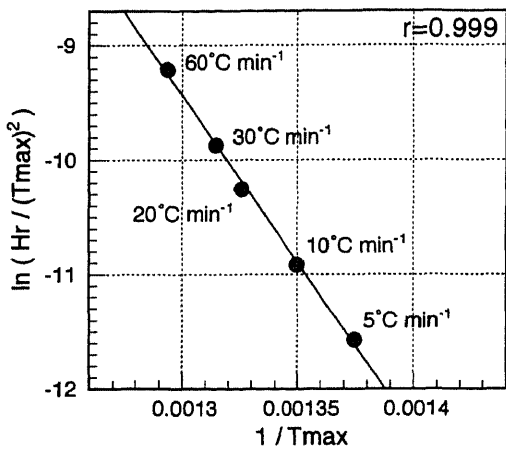
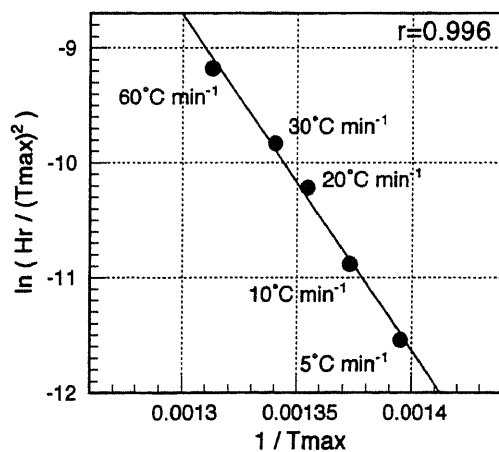d) Phenol

$\ln (Hr / (Tmax)^2) = -3.06 \times 10^4 (1 / Tmax) + 30.8$
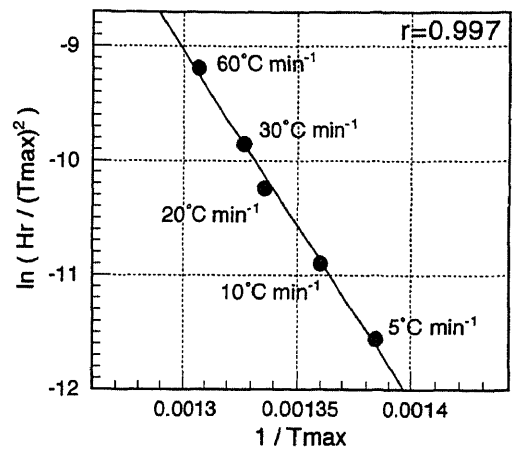
e) Heptane

$\ln (Hr / (Tmax)^2) = -2.80 \times 10^4 (1 / Tmax) + 27.5$
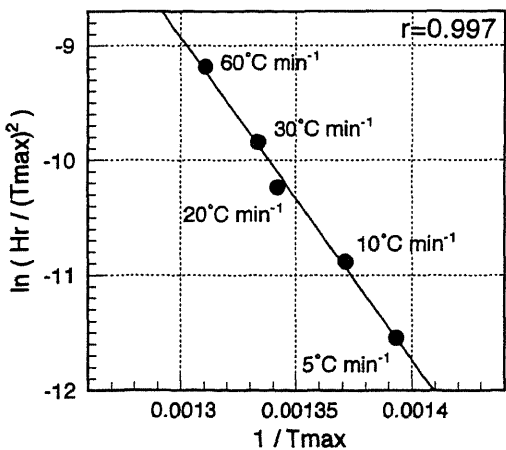
f) Indene

$\ln (Hr / (Tmax)^2) = -2.77 \times 10^4 (1 / Tmax) + 26.6$
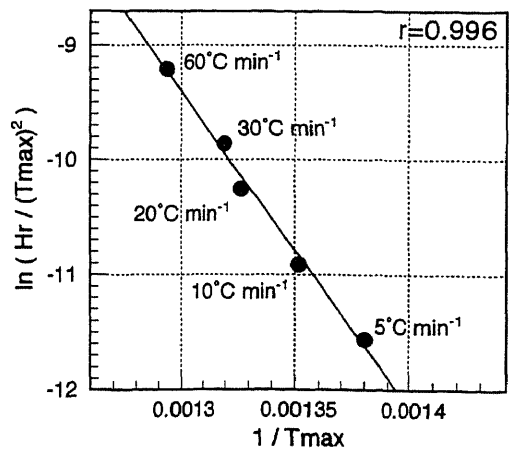
Fig. 3-9. $1/ T_{max}$ - ln $(Hr/(T_{max})^2)$ plots of benzene (a), hexane (b), toluene (c), phenol (d), heptane (e) and indene (f) on the release from kerogen sample No. 90101.

a) Benzene

$\ln (Hr / (Tmax)^2) = -2.39 \times 10^4 (1 / Tmax) + 21.2$

b) Hexane

$\ln (Hr / (Tmax)^2) = -2.57 \times 10^4 (1 / Tmax) + 23.8$
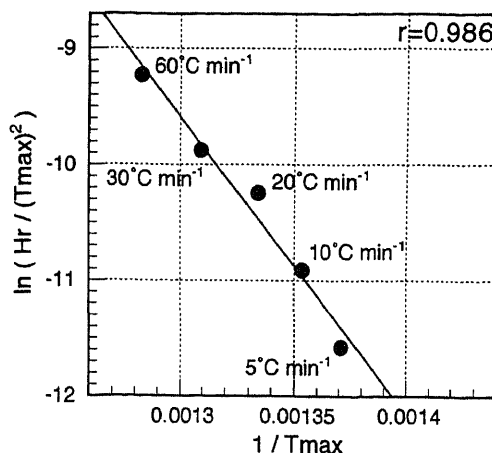
c) Toluene

$\ln (Hr / (Tmax)^2) = -2.48 \times 10^4 (1 / Tmax) + 22.4$
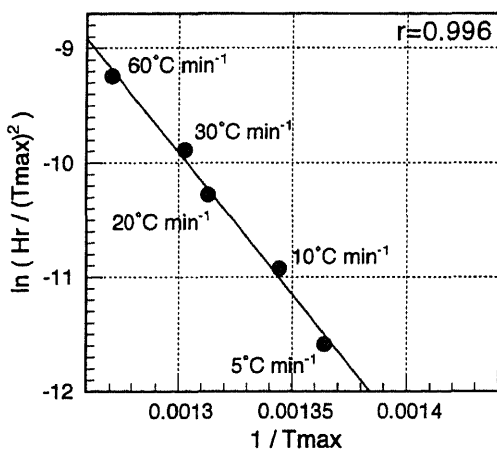
d) Phenol

$\ln (Hr / (Tmax)^2) = -2.54 \times 10^4 (1 / Tmax) + 23.5$
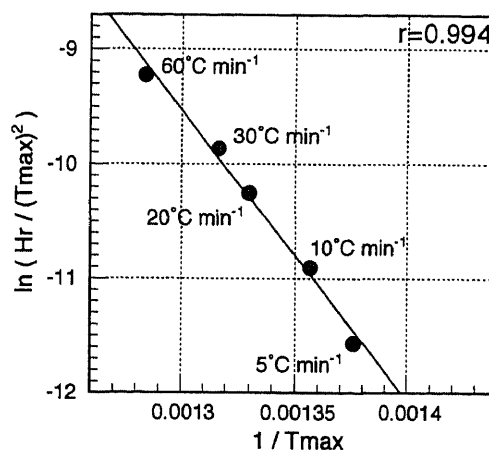
e) Heptane

$\ln (Hr / (Tmax)^2) = -2.72 \times 10^4 (1 / Tmax) + 26.0$
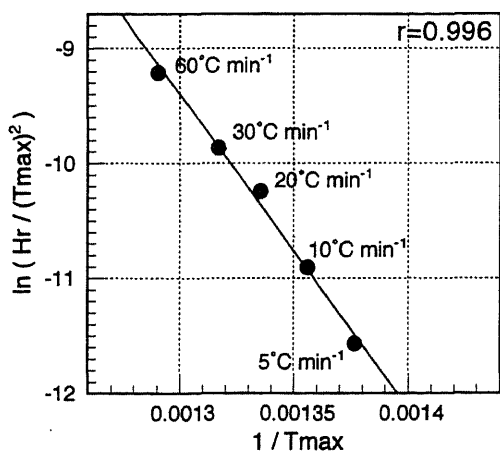
f) Indene

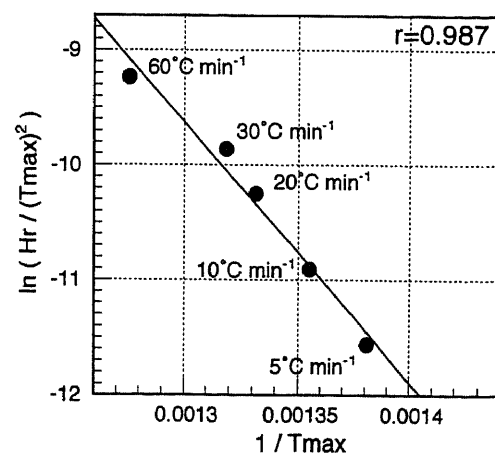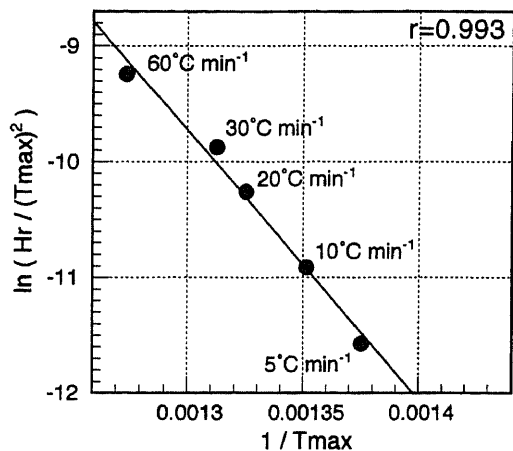$\ln (Hr / (Tmax)^2) = -2.30 \times 10^4 (1 / Tmax) + 19.9$
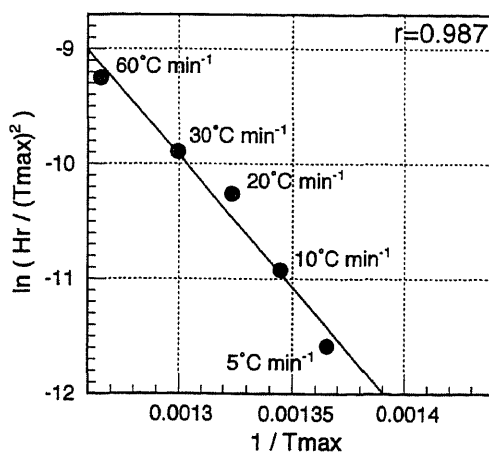
Fig. 3-10. $1/ T_{max}$ - $\ln (Hr/(T_{max})^2)$ plots of benzene (a), hexane (b), toluene (c), phenol (d), heptane (e) and indene (f) on the release from kerogen sample No. 90104.
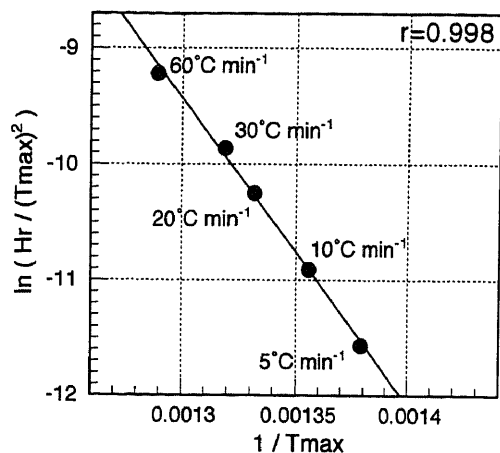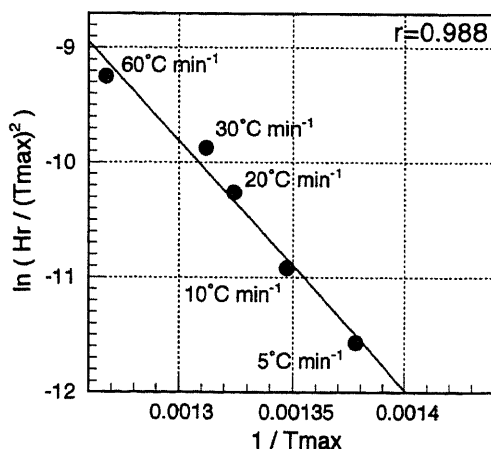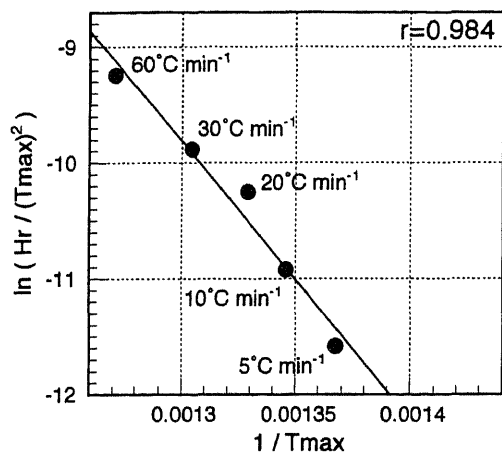
Table 3-2. Activation energies, pre-exponential factors and rate constants at 120°C of benzene, hexane, toluene, phenol, heptane, and indene on release from kerogen samples in the Shinjo sediments.

m/z	Compounds	Kerogen	Activation energies kcal / mol	Pre-exponential factors s^{-1}	Rate constants at 120°C s^{-1}
78	Benzene	83109	47.0	1.03×10^{12}	7.65×10^{-15}
		83105	49.7	4.37×10^{12}	1.02×10^{-15}
		83101	46.3	3.24×10^{11}	5.90×10^{-15}
		90101	54.3	9.35×10^{13}	6.07×10^{-17}
		90104	47.5	6.62×10^{11}	2.59×10^{-15}
		average	49.0	2.46×10^{12}	1.41×10^{-15}
86	Hexane	83109	58.5	4.76×10^{15}	1.43×10^{-17}
		83105	56.1	4.80×10^{14}	3.11×10^{-17}
		83101	52.6	3.12×10^{13}	1.79×10^{-16}
		90101	58.3	1.88×10^{15}	7.29×10^{-18}
		90104	51.0	8.87×10^{12}	3.94×10^{-16}
		average	55.3	2.60×10^{14}	4.69×10^{-17}
92	Toluene	83109	46.4	6.01×10^{11}	9.62×10^{-15}
		83105	51.4	1.41×10^{13}	3.75×10^{-16}
		83101	47.3	6.65×10^{11}	3.36×10^{-15}
		90101	58.0	1.20×10^{15}	6.83×10^{-18}
		90104	49.4	2.19×10^{12}	7.53×10^{-16}
		average	50.5	6.83×10^{12}	5.75×10^{-16}
94	Phenol	83109	53.6	2.29×10^{14}	3.64×10^{-16}
		83105	48.8	2.83×10^{12}	2.10×10^{-15}
		83101	50.2	5.73×10^{12}	7.08×10^{-16}
		90101	60.9	1.21×10^{16}	1.68×10^{-18}
		90104	50.4	6.60×10^{12}	6.31×10^{-16}
		average	52.8	4.95×10^{13}	2.19×10^{-16}
100	Heptane	83109	52.0	9.19×10^{13}	1.13×10^{-15}
		83105	58.0	2.47×10^{15}	1.41×10^{-17}
		83101	53.3	6.67×10^{13}	1.56×10^{-16}
		90101	55.7	4.13×10^{14}	4.47×10^{-17}
		90104	54.0	8.51×10^{13}	8.11×10^{-17}
		average	54.6	2.21×10^{14}	9.77×10^{-17}
116	Indene	83109	44.8	1.94×10^{11}	2.41×10^{-14}
		83105	44.9	1.46×10^{11}	1.59×10^{-14}
		83101	43.1	3.56×10^{10}	3.89×10^{-14}
		90101	55.0	1.64×10^{14}	4.35×10^{-17}
		90104	45.6	1.71×10^{11}	7.62×10^{-15}
		average	46.7	4.90×10^{11}	5.34×10^{-15}

3.89 x 10^{-14} s^{-1} for indene from No. 83101 and 1.68 x 10^{-18} s^{-1} for phenol from No. 90101, respectively. The average values of the rate constants of each compound from five kerogen samples were in order of indene > benzene, toluene > phenol >, hexane, heptane, whereas the average activation energies were inverse in order (Table 3-2). In this study, it is considered that the activation energy is the amount of energy required to break bonds. Therefore, it is hypothesized that hexane and heptane of aliphatic hydrocarbons are more strongly bound to kerogen than benzene, toluene and indene of aromatic hydrocarbons based on their higher activation energies and slower decomposition rates.

Determination of activation energies and pre-exponential factors by the Rock-Eval pyrolysis has been performed on numerous samples. A narrow range of activation energies between 49 kcal/mol (Zumberge *et al.*, 1988) and 56 kcal/mol (Ungerer and Pelet, 1987; Jarvie, 1991; Tegelaar and Noble, 1994) was found for organic compounds from the Type I kerogen. Tissot *et al.* (1987) reported 56 kcal/mol and the pre-exponential factors in a range of 10^{14} s^{-1} to 10^{18} s^{-1} for the Type I kerogen. The ranges were somewhat wider for marine kerogen (Type II) with activation energies and pre-exponential factors, 46 kcal/mol and 1.1 x 10^{12} s^{-1} (Novelli *et al.*, 1987), 53 kcal/mol and 9.7 x 10^{13} s^{-1} (Jarvie, 1991), and 56 kcal/mol and 5.2 x 10^{14} s^{-1} (Espitalié *et al.*, 1988), respectively. The high sulfur kerogens in carbonate and sulfur-rich source rocks were reported to have lower activation energies than marine shales (Tissot *et al.*, 1987; Tegelaar and Noble, 1994). Furthermore, the high oxygen and sulfur kerogens have lower activation energies than the high sulfur only kerogens (Jarvie and Lundell, 2001). Activation energies and pre-exponential factors for the Type III kerogen (low maturity coals) were from 47 to 60 kcal/mol, and from 10^{13} to 10^{16} s^{-1} (Ungerer *et al.*, 1986). Elemental compositions of kerogens in Neogene Shinjo sediments plotted on a Van

Krevelen diagram indicate that they are a mixture of the Type II and III kerogens (Taguchi *et al.*, 1986). The activation energies and pre-exponential factors obtained in this study, therefore, fall within the range of reported values for bulk kerogen of Type II and III.

The bulk kinetic parameters for thermal decomposition of kerogen obtained by Rock-Eval pyrolysis are of practical use in petroleum exploration, probably because they are averaged values of compound mixtures. However, it is better to know precise activation energies and pre-exponential factors of individual compounds not only for academic studies, but also for the petroleum exploration. Since the combined method of TG-GC/MS and TG-MS enables to estimate the activation energy and pre-exponential factor of an individual compound on the release from kerogen, this method gives detailed and useful information on the timing of petroleum generation and the quality of petroleum.

CONCLUSIONS

To determine values of kinetic parameters for individual organic compounds on the release from kerogen, five kerogen samples of different burial depth from Neogene Shinjo sediments were heated in TG from room temperature to 800°C at increasing rate of 5, 10, 20, 30 and 60 °C min^{-1}, and released compounds were analyzed by GC/MS and compound release profiles by MS. The results of these analyses are summarized as follows:

1. The large peaks at about 500 °C on the compound release profiles of m/z 78, 86, 92, 94, 100, and 116 by the TG-MS analysis were found and they were of benzene, hexane, toluene, phenol, heptane, and indene released from kerogen, respectively.

2. T_{max} of compounds released from kerogen samples shifted towards higher temperature with temperature increasing rate, and fell in a range between 424.6 °C (heptane at 5 °C min^{-1}) and 516.9 °C (indene at 60 °C min^{-1}).

3. The plot of $1/T_{max}$ vs. ln $(Hr/(T_{max})^2)$ for each compound on release showed a reasonably straight line with a high correlation coefficiency.

4. As a result of determination of the kinetic parameters of an individual compound on release from kerogens by the equation of Braun and Burnham (1987), it was found that the activation energies and pre-exponential factors fell in a range between 43.1 kcal/mol (indene) and 60.9 kcal/mol (phenol), and between 3.56 x 10^{10} s^{-1} (indene) and 1.21 x 10^{16} s^{-1} (phenol), respectively.

5. The average values of these kinetic parameters had decomposition rates in order of indene > benzene, toluene > phenol > hexane, heptane. Therefore, it was found that hexane and heptane were more strongly bound with kerogen matrix than benzene,

toluene and indene.

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Chapter 4

Mathematical Model for Release of Compounds from Kerogen

and its Application for Neogene Sediments of the Shinjo Basin, Japan

ABSTRACT - A mathematical model was made to obtain depth profiles of compound abundances (release extents) released from thermal decomposition of kerogen in a sedimentary sequence using parameters for reaction kinetics in the decomposition and for thermal history of the sequence. Equations for release extents and differential release extents of compounds were derived from a rate law of first-order reaction and the Arrhenius expression. The model was applied for the Neogene Shinjo sediments, whose depths were reported by Taguchi *et al.*, (1986). The activation energies and pre-exponential factors for benzene, hexane, toluene, phenol, heptane and indene on release from kerogen were reported in chapter 3. The geothermal gradient was determined by the method by Suzuki (1984) and data by Suzuki and Shimada (1983), and the rate of the sediment subsidence by Shiraishi and Matoba (1992). The depth profiles of differential release extents for compounds were different in temperature (therefore, depth) each other. The average temperatures of the maximum releases were 134°C for benzene, 159°C for hexane, 136°C for toluene, 143°C for phenol, 152°C for heptane, and 121°C for indene. The temperatures for benzene, toluene and indene appear in the petroleum generation zone and for the rests below the zone. Furthermore, the model indicated that hexane and heptane of aliphatic hydrocarbons were released in sediments deeper than benzene, toluene and indene of aromatic ones. These depth profiles was similar in pattern to those reported for solvent extractable aliphatic and aromatic hydrocarbons in the sediments, but shifted toward deeper sediments than the reported profiles. These shifts may be corrected by taking consideration of the effect of sediment constituents for the determination of parameters for reaction kinetics.

INTRODUCTION

Reaction kinetics have been applied for the generation of petroleum constituents in sediments, using parameters such as activation energies and pre-exponential (frequency) factors for thermal decomposition of kerogen (Tissot, 1969; Tissot and Espitalié, 1975; Ungerer et al., 1986; Sweeney et al., 1986). For determination of the two parameters, the Rock-Eval pyrolysis method (Ungerer et al., 1986; Tissot et al., 1987; Burnham et al., 1987; Ungerer and Pelet, 1987; Sweeney et al., 1990; Jarvie, 1991) and the programmed micropyrolysis method (Burnham and Braun, 1990; Braun et al., 1991) have been used widely. These pyrolysis methods give three peaks by detection, which correspond to those for hydrocarbons in free form, hydrocarbons released from kerogen, and CO_2 from kerogen. Since the first two peaks include mixtures of compounds, the two methods give only average values of activation energies and pre-exponential factors for the compounds in the mixtures.

For identification of individual compounds thermally released from kerogen and for determination of their release temperatures, a thermogravimetric analyzer (TG) was connected to a gas chromatograph-mass spectrometer (GC/MS) and to a mass spectrometer (MS), respectively (in Chapter 2). Furthermore, this system enables to determine activation energies and pre-exponential factors for individual compounds on release from kerogen by changing the increasing rate of temperature in TG, and the author obtained individual activation energies and pre-exponential factors for six compounds on release from kerogen samples recovered from the Neogene Shinjo sediments (in Chapter 3).

In this Chapter, the author used a mathematical model to know release extents of

individual compounds from kerogen along with progressively increasing temperature of sediments, using parameters such as activation energy and pre-exponential factor for reaction kinetics and temperature and rate of subsidence for thermal history of sediments. Here the author describes the results of the application of the model to the stratigraphic sequence of the Neogene Shinjo sediments and compare the results to the depth profiles of solvent extractable hydrocarbons reported for the sediments.

METHODS

Mathematical Model

A mathematical model for describing the thermal decomposition of kerogen was first introduced by Tissot (1969) and further described by Tissot and Espitalié (1975) and by Tissot and Welte (1984). Since the models regard kerogen as a composite of various kinds of molecular species, its thermal decomposition is treated by a set of several first-order reactions with different activation energies and pre-exponential factors, occurring simultaneously and individually.

When a release reaction for a compound from kerogen can be approximated as a first-order reaction, the reaction rate

$$\frac{dN_b}{dt} = -kN_b \tag{1}$$

where k is a reaction rate constant and N_b is an amount of a kerogen-bounded compound at time t. The temperature dependence of the rate constant is given by the Arrhenius expression

$$k = Ae^{-E/RT} \tag{2}$$

where A is a pre-exponential factor, E an activation energy, R the ideal gas constant, and T temperature in K for a compound on release from kerogen.

From (1) and (2)

$$\frac{dN_b}{N_b} = -Ae^{-E/RT}dt \tag{3}$$

By the analysis of n-alkanes in sediments at several different depths, Philippi (1965) showed that time and temperature of subsiding sediments are important factors in petroleum generation. Therefore, in order to make a mathematical model for

hydrocarbon generation by thermal decomposition of kerogen during diagenesis, it is necessary to interrelate time t, temperature T, and depth d (m) of a subsidizing sediment as reported by Johns and Shimoyama (1972).

From a paleo-geothermal gradient u (K m^{-1}) and a surface temperature Ts (K),

$$T = ud + Ts \qquad (4)$$

From a rate of subsidence v (m s^{-1})

$$d = vt \qquad (5)$$

Combining (4) and (5)

$$t = \frac{1}{uv}(T - Ts) \qquad (6)$$

Combining (3) and (6)

$$\frac{dN_b}{N_b} = -\frac{1}{uv}Ae^{-E/RT}dT \qquad (7)$$

Integral of (7)

$$\ln N_b = -\frac{1}{uv}A\int_{Ts}^{T}e^{-E/RT}dT + const \qquad (8)$$

When $T = Ts$, $N_b = N_0$ (initial amount) and $const = \ln N_0$.

Hence,

$$\ln\frac{N_b}{N_0} = -\frac{1}{uv}A\int_{Ts}^{T}e^{-E/RT}dT$$

$$\frac{N_b}{N_0} = \exp\left(-\frac{1}{uv}A\int_{Ts}^{T}e^{-E/RT}dT\right) \qquad (9)$$

An amount of a released compound (N_r)

$$N_r = N_0 - N_b \qquad (10)$$

Combining (9) and (10)

$$\frac{N_r}{N_0} = 1 - \exp\left(-\frac{1}{uv}A\int_{Ts}^{T}e^{-E/RT}dT\right) \qquad (11)$$

Differentiation of equation (11) with respect to T leads to the following equation, which denotes the change in rate of release with progressively increasing temperature:

$$\frac{d(N_r/N_0)}{dT} = \left[\frac{N_b}{N_0}\right]\left(\frac{1}{uv}Ae^{-E/RT}\right)$$

(12)

Solving equations (11) and (12) by using the experimentally determined parameters for reaction kinetics and thermal history of sediments, we can obtain a depth profile of release extent (Eq (11)) and differential release extent (Eq (12)) for a compound from kerogen.

Parameters for Shinjo sediments

Activation energy and pre-exponential factor

In Chapter 3, the activation energies and pre-exponential factors for six organic compounds on release from five kerogen samples recovered from the Neogene Shinjo sediments of different burial depth were determinated.

Kerogen sample Nos. 83109, 83105 and 83101 occurred in sediments above the threshold of intense petroleum generation (Shimoyama and Matsubaya, 1985; Taguchi *et al.*, 1986). Therefore, these kerogens are rather immature and can still generate organic compounds by heating. Values of activation energies and pre-exponential factors with their averages for these three kerogen samples are listed in Table 4-1, and used in this study.

Paleo-geothermal gradient and rate of subsidence

Suzuki (1984) reported the method of determination of the maximum temperatures experienced by sediments, using the ratios of $20S/20R$ of C_{29}-steranes and of $22S/22R$ of C_{32}-hopanes. From the S/R ratios of steranes and hopanes in the Shinjo sediments

Table 4-1. Activation energies and pre-exponential factors for compounds on release from kerogen and characterization of depth profiles of differential release extents of those compounds from kerogen by temperature.

m/z	Compounds	Kerogen	Activation energy kcal / mol	Pre-exponential factor s^{-1}	Onset of release[1] °C	Maximum release °C	Ending of release[1] °C
78	Benzene	83109	47.0	1.03×10^{12}	103	128	140
		83105	49.7	4.37×10^{12}	116	141	153
		83101	46.3	3.24×10^{11}	104	130	142
		average	47.7	1.13×10^{12}	108	134	146
86	Hexane	83109	58.5	4.76×10^{15}	140	164	176
		83105	56.1	4.80×10^{14}	136	161	173
		83101	52.6	3.12×10^{13}	126	152	164
		average	55.7	4.15×10^{14}	134	159	171
92	Toluene	83109	46.4	6.01×10^{11}	101	127	139
		83105	51.4	1.41×10^{13}	122	147	159
		83101	47.3	6.65×10^{11}	108	134	146
		average	48.4	1.78×10^{12}	111	136	149
94	Phenol	83109	53.6	2.29×10^{14}	122	147	158
		83105	48.8	2.83×10^{12}	111	137	149
		83101	50.2	5.73×10^{12}	118	143	156
		average	50.9	1.55×10^{13}	117	143	154
100	Heptane	83109	52.0	9.19×10^{13}	116	140	151
		83105	58.0	2.47×10^{15}	140	165	176
		83101	53.3	6.67×10^{13}	127	152	164
		average	54.4	2.47×10^{14}	128	152	164
116	Indene	83109	44.8	1.94×10^{11}	95	121	133
		83105	44.9	1.46×10^{11}	97	123	136
		83101	43.1	3.56×10^{10}	91	117	129
		average	44.3	1.00×10^{11}	95	121	133

1) Temperature at the 5% level on the base of the maximum release set 100%

(Suzuki and Shimada, 1983), we obtained the maximum temperatures of the sediments. Plotting these temperatures against the depths of sediments (Taguchi *et al.*, 1986), we obtained a nearly straight line (Fig. 4-1a). Using a least squares method, we determined a value of 3.6 K/100 m for a paleo-geothermal gradient. The average paleo-geothermal gradient and average surface temperature in Neogene argillaceous sediments of Japan have been estimated to be 3.25 K/100 m and 288 K (15°C), respectively (Aoyagi and Kazama, 1980). The value (3.6 K/100 m) is close to the average value. A sedimentary sequence has its own paleo-geothermal gradient and rate of subsidence, which are not fixed through the process of diagenesis. However, the increasing rate of temperature (3.6 K/100 m) was used together with 288K for the surface temperature in this study.

The boundary age of the Nakawatari and Noguchi Formations was estimated to be 3.6 Ma, the Noguchi and Furukuchi Formations 4.2 Ma, the Furukuchi and Kusanagi Formations 9.2 Ma, and the Kusanagi and Osawa Formations 12.9 Ma (Shiraishi and Matoba, 1992). Using these ages and the depths of the boundaries as shown in Fig. 4-1b, the average value of the rate of subsidence was calculated to be 159 m/Ma (100 m/0.63 Ma). The value for the Onnagawa Formation in Akita basin, which corresponds to the Kusanagi Formation, is 100 – 145 m/Ma (Suzuki, 1979). This value is close to the calculated one (159 m/Ma) for the Shinjo sediments.

Hence, equations (11) and (12) for the Shinjo sediments are expressed, respectively, as

$$\frac{N_r}{N_0} = \exp\left(-5.5 \times 10^{12} A \int_{288}^{T} e^{-E/RT} dT\right) \qquad (11)'$$

and

$$\frac{d(N_r/N_0)}{dT} = \left[\frac{N_b}{N_0}\right]\left(5.5 \times 10^{12} A e^{-E/RT}\right) \qquad (12)'$$

Maximum temperature / °C

80   100   120   140

a)

0 m
100

500
Sediment
thickness
scale

Age / Ma

0   5   10   15

b)

Nakawatari Formation		83110
		83109
Noguchi Formation		83108 83107 83106
Furukuchi Formation		83105 83104
		83103
Kusanagi Formation	upper	83102
		83101
		83003 83002 83001
	middle	90101
		90102
		90103
	lower	90104 90105
Okawa Formation		

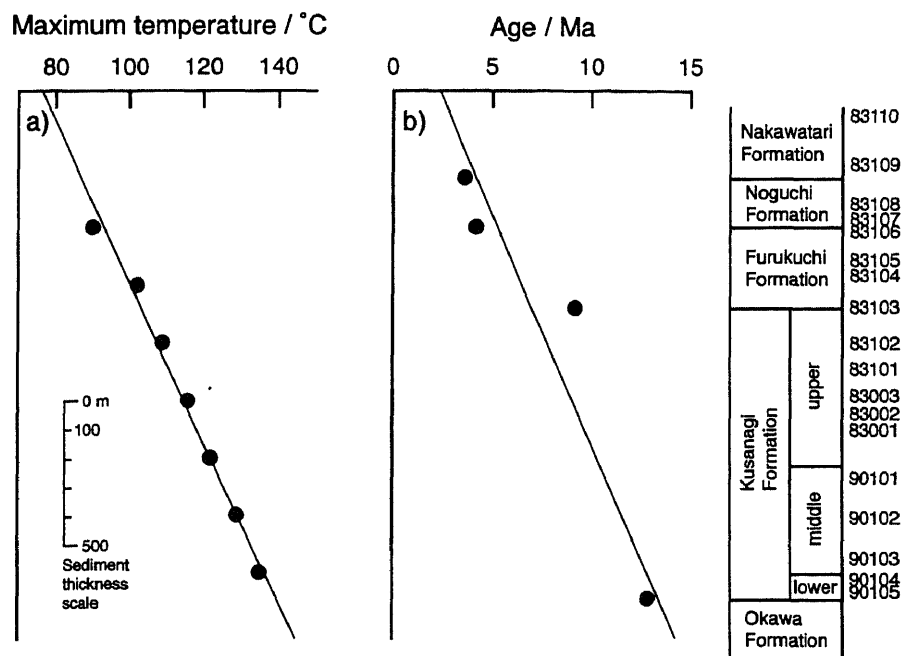Fig. 4-1. Thermal gradient (a) and rate of subsidence (b) of the Neogene Shinjo sediments. Maximum temperatures were determined by the method by Suzuki (1984) and data by Suzuki and Shimada (1983). The depth used were from Taguchi *et al.*, (1986) and the ages from Shiraishi and Matoba (1992).

Mathematica Version 3.0 (Wolfram Research Inc.) was used for calculations of the release extents and the differential release extents.

RESULTS AND DISCUSSION

Depth profiles by model

Figure 4-2 shows the depth profiles of differential release extents for benzene, hexane, toluene, phenol, heptane and indene obtained by the equation (12)'. The three profiles in thin line for each compound were obtained by using activation energies and pre-exponential factors for the three kerogen samples, and that in thick line was for the average of the three (Table 4-1). The three profiles for a compound are similar to each other in pattern but different in temperature.

The average temperatures of maximum release were $134°C$ for benzene, $159°C$ for hexane, $136°C$ for toluene, $143°C$ for phenol, $152°C$ for heptane, and $121°C$ for indene (Table 4-1). The temperatures of onset, maximum and ending of release in each profile are shown in Table 4-1, when the onset and the ending were defined at the 5% level on the base of the maximum release 100%. Hexane and heptane of aliphatic hydrocarbons were found to be released at deeper depth than benzene, toluene and indene of aromatic hydrocarbons, mainly because of their higher activation energies than those of the three aromatic ones. The differences of average values in temperature between the onset and the maximum of the six compounds were 24 to $26°C$, and between the maximum and the ending were 11 to $13°C$, showing the formers were twice broader in temperature than the latters. This is due to the fact that release reactions become faster as temperature become higher.

A dashed line is drawn indicating the temperature of $120°C$ at the sediment No. 83001 in Fig. 4-2. The joint study on the organic and inorganic diagenesis in this sequence concluded that petroleum generation took place mainly in the upper part of
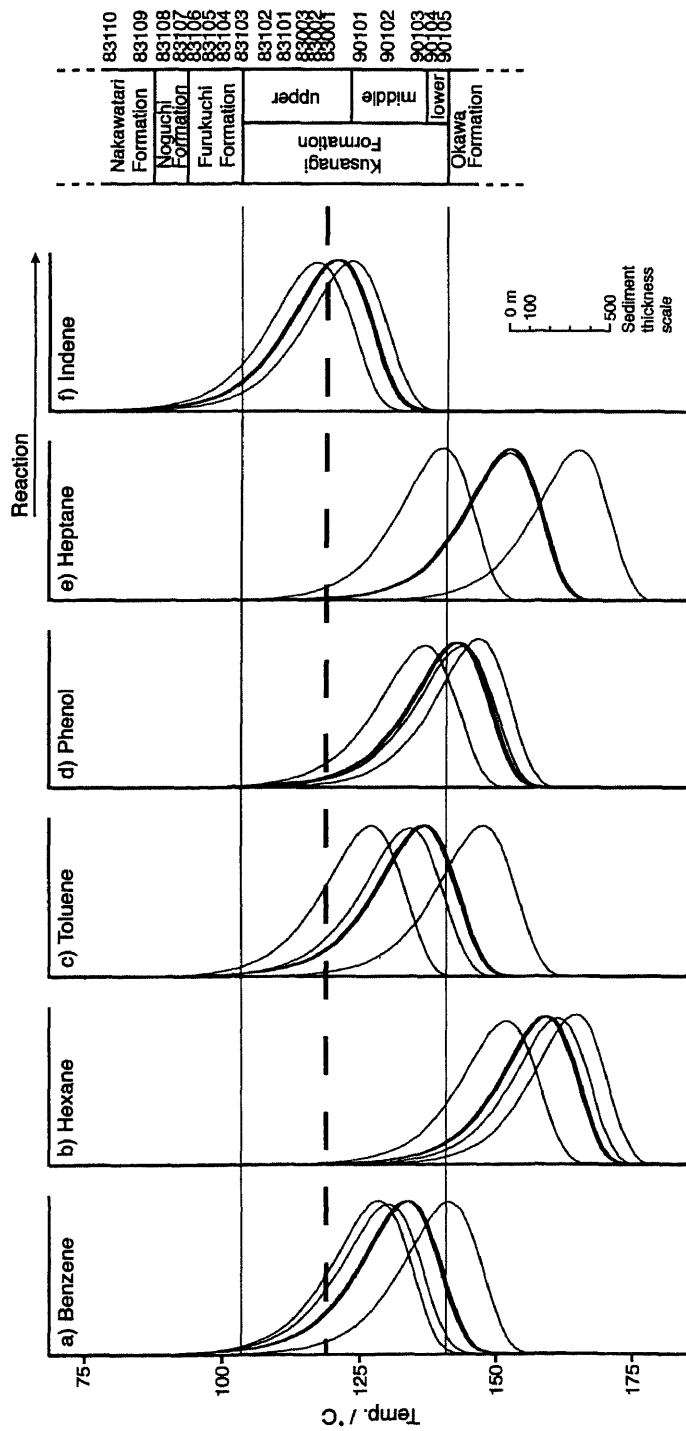
Fig. 4-2. Depth profiles of differential release extents of benzene (a), hexane (b), toluene (c), phenol (d), heptane (e) and indene (f) obtained by the mathematical model.

the Kusanagi Formation with the onset of the intense generation at 120°C (Taguchi *et al.*, 1986). The average profiles show that indene was released within the Kusanagi Formation with the maximum release around the dashed line. Most of benzene and toluene were released within the formation, but their maximum releases were at 14°C and 16°C, respectively, below the line. Roughly a half of phenol was released within the formation, but the rest in the lower formation. The large part of hexane and heptane was released not in Kusanagi Formation but in the lower formation.

Comparison of model with reported studies

Figure 4-3a shows the depth profiles of release extents of benzene, toluene and indene of aromatic hydrocarbons obtained from the equation (11)'. Figure 4-3b shows the depth profiles of the concentrations of naphthalene, 2-methylnaphthalene and 1,6-dimethylnaphthalene in bitumen in the Shinjo sediments (Shimoyama *et al.*, 2000). Other solvent extractable methyl- and dimethylnaphthalenes also showed similar depth profiles, whose concentrations increased at the Furukuchi Formation and became maximum in the upper part of the Kusanagi Formation (especially, No. 83003). Likewise, it was reported that the depth profiles of the concentrations of aromatic hydrocarbons, such as alkylbenzenes and alkylnaphthalenes, showed their maximum in the upper part of the Kusanagi Formation (Shioya and Ishiwatari, 1983). In comparison, the release extent of indene by the model may explain the reported profiles of those extractable hydrocarbons. However, those of benzene and toluene do not properly explain the profiles of the reported ones, because the model showed the releases slightly at deeper sediments.

Figure 4-3c shows the depth profiles of release extents of hexane and heptane of aliphatic hydrocarbons. The releases of these aliphatic hydrocarbons started around the
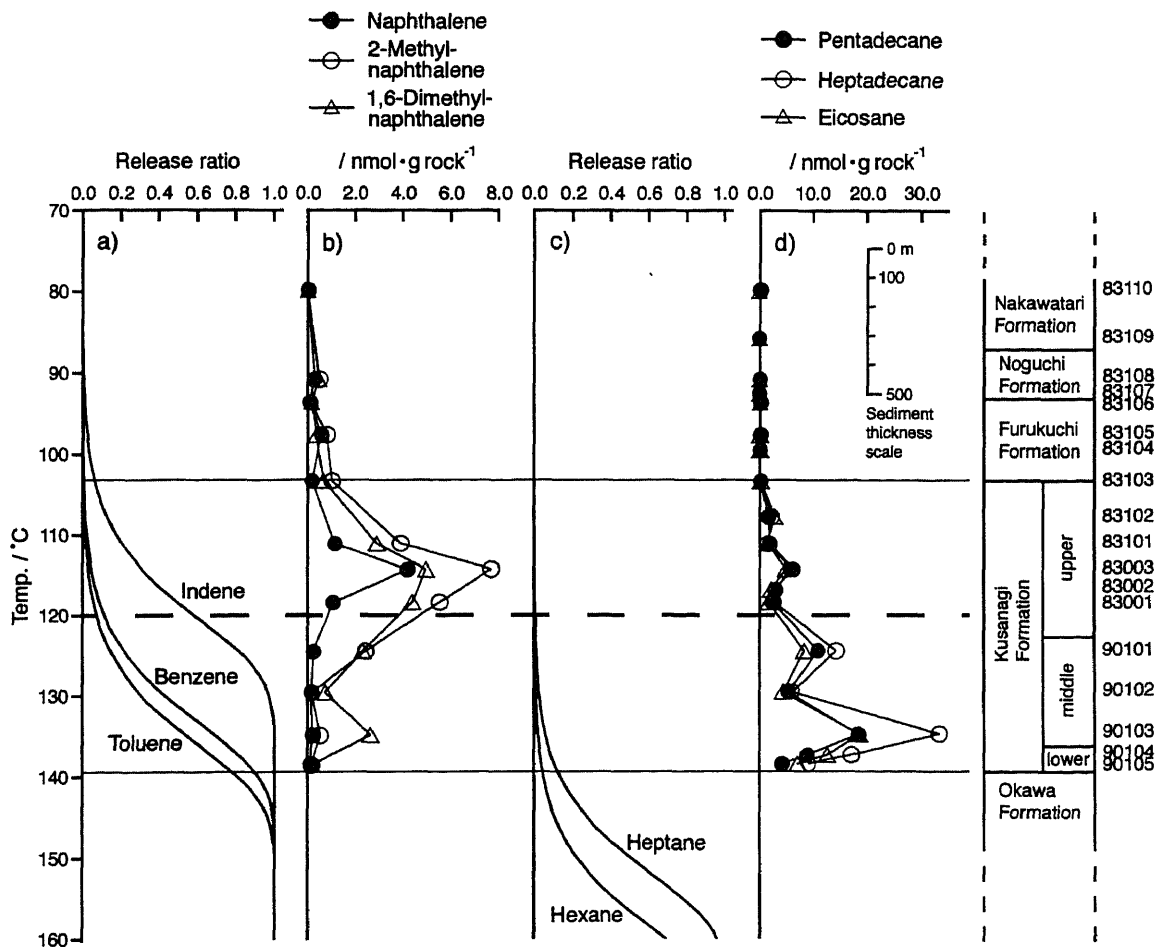
Fig. 4-3. Depth profiles of release extents of benzene, toluene and indene by the mathematical model (a), depth profiles of naphthalene, 2-methylnaphthalene and 1,6-dimethylnaphthalene in the Neogene Shinjo sediments (Shimoyama *et al.*, 2000) (b), depth profiles of release extents of hexane and heptane by the model (c), and depth profiles of pentadecane, heptadecane and eicosane in the Neogene Shinjo sediments (Yabuta *et al.*, 2002) (d).

upper and middle parts of the Kusanagi Formation. Figure 4-3d shows the depth profiles of the concentrations of aliphatic hydrocarbons such as pentadecane, heptadecane and eicosane in bitumen in the Shinjo sediments (Yabuta, et al., 2002). The concentrations of these aliphatic hydrocarbons started increasing at the upper part of the Kusanagi Formation, and increased with depth. Similar depth profiles were observed with n-alkanes (C_{12} - C_{38}), pristane and phytane (Ishiwatari and Shioya, 1986). The release extents of the two compounds by the model started at deeper sediments than those of extractable aliphatic hydrocarbons. One of possible explanations for the difference is that hexane and heptane in the model are lower molecular weight aliphatic hydrocarbons than the reported extractable hydrocarbons. Activation energies of lower molecular weight aliphatic hydrocarbons in thermal decomposition of kerogen are higher than those of higher molecular weight ones (Tang and Stauffer, 1994; Tang and Béhar, 1995; Béhar et al., 1997). Therefore, the extractable hexane and heptane in the sediments, if analyzed, may show the depth profile shifted towards lower sediments than those of the reported hydrocarbons.

The concentrations of reported solvent extractable aromatic and aliphatic hydrocarbons decreased below No. 83001 (Fig. 4-3b) and No. 90104 (Fig. 4-3d), respectively. Three possible explanations can be proposed for the decreases. 1) Kerogen in the sediment Nos. 83001 and 90104 and below contained less aromatic and aliphatic hydrocarbon moieties than those above the sediment Nos. 83001 and 90104, respectively. 2) Aromatic and aliphatic hydrocarbons generated from kerogen in sediments below Nos. 83001 and 90104, respectively, had migrated from those sediments together with interstitial water. 3) Aromatic and aliphatic hydrocarbons generated in sediments below Nos. 83001 and 90104, respectively, decomposed because of the higher temperature of these sediments than those above Nos. 83001 and

90104. It seems that the explanation 3) is the least likely one, because aromatic hydrocarbons are thermally more stable than aliphatic ones. The explanation 1) is most likely. If so, it is necessary for this model to include another factor to evaluate release extents quantitatively with depth of sediments for reconstructions of the reported profiles of aromatic hydrocarbons below No. 83001 and aliphatic ones below No. 90104. Therefore, the profiles of the reported compounds (Fig. 4-3b and d) should be used down to their depth of maximum concentrations for a comparison with those of the model in Fig. 4-3a and c, respectively. In addition, the author assumed that the reported extractable compounds have been generated by thermal decomposition of kerogen like by this model. This assumption is not necessarily effective to all extractable compounds.

Catalytic effect to kinetic parameters

The author used the kinetic parameters obtained from kerogen samples separated from sediments, and therefore, the catalytic effect by the sediment constituents was not counted in the model. The catalytic effect by the sediment constituents is possible to make different depth profiles from those by the model. The sediments in the upper sequence (from the Nakawatari to the Furukuchi Formations) contain appropriate concentrations of clay minerals, especially smectite, and ones in the lower sequence (the Kusanagi Formation) contain a mixed-layer illite/smectite mineral (50/50% to 70/30%) (Taguchi et al., 1986). The illite/smectite mineral has been known to be formed from smectite by the addition of alkali cations during sediment diagenesis (Burst, 1969; Perry and Hower, 1972). This indicates that the Kusanagi Formation had previously contained enough smectite. It has been pointed out that catalysis by minerals, particularly clay minerals, was responsible for the low measured pseudo-activation

energies (Brooks, 1948; Dobryansky, 1963; Hedberg, 1964; Louis, 1966; Tissot, 1969; Shimoyama and Johns, 1971; Welte, 1972). Therefore, if the kinetic parameters were obtained by heating experiments of sediment samples containing kerogen, the overall depth profiles probably shift upwards along the sequence.

CONCLUSIONS

A mathematical model for compound release from kerogen was made using kinetic parameters such as activation energy and pre-exponential factor and thermal history parameters such as geothermal gradient and rate of sediment subsidence. The model was applied for the Neogene Shinjo sediments, using the activation energies and pre-exponential factors for six compounds, and the geothermal gradient and the rate of the sediment subsidence.

The depth profiles of differential release extents of benzene, hexane, toluene, phenol, heptane and indene from kerogen differed each other. Their maximum releases were found around 134°C for benzene, 159°C for hexane, 136°C for toluene, 143°C for phenol, 152°C for heptane and 121°C for indene.

The concentrations of reported extractable aliphatic hydrocarbons in Shinjo sediments increased at deeper sediments than those of extractable aromatic ones, which coincide with the results obtained by the model. However, there is a depth difference between those by the model and the reported studies, the model showing the depth profiles deeper than the reported extractable compounds. This difference may be corrected by the consideration of catalytic effect of the sediment constituents, especially clay minerals, to the kinetic parameters for thermal decomposition of kerogen.

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Chapter 5

Summary and Conclusions

Kerogen accounts for a major portion of sedimentary organic matter and is important to the study of organic diagenesis and petroleum generation. Some studies described the petroleum generation from kerogen by kinetic models using data obtained by heating experiments such as the Rock-Eval pyrolysis (Ungerer *et al.*, 1986; Tissot *et al.*, 1987; Burnham *et al.*, 1987; Ungerer and Pelet, 1987; Sweeney *et al.*, 1990; Jarvie, 1991) and programmed micropyrolysis methods (Burnham and Braun, 1990; Braun *et al.*, 1991). Since the products released from kerogen using these methods are a mixture of compounds, activation energies and pre-exponential factors for individual compounds released from kerogen can not be determined. It is better to know precise activation energies and pre-exponential factors of individual compounds not only for academic studies, but also for the petroleum exploration. Therefore, the author performed laboratory heating experiments to kerogen using TG-GC/MS and TG-MS methods in order to reveal the kind of released compounds and the changes of release-temperatures of compounds from kerogen by diagenesis and obtain the activation energy and pre-exponential factor for individual compounds in this study. Furthermore, the release extents of individual compounds by kerogen diagenesis were estimated by a mathematical model using these parameters and temperature and rate of subsidence for thermal history of sediments.

Kerogens of different burial depth from Neogene Shinjo sediments were heated in the TG from room temperature to 800°C under a helium flow, and released compounds were analyzed by GC/MS or MS.

Kerogen samples released various kinds of organic compounds during the heating. Among 249 compounds identified, aliphatic and aromatic hydrocarbons were major compounds. These compounds were also found as major compounds in petroleum.

Therefore, the result supports that petroleum hydrocarbons were generated from kerogen during diagenesis in the sediments. Examination of continuous release profiles of individual compounds from kerogen along heating temperature showed that compound releases started at around 350 °C and ended at roughly 550 °C with maximum-release at 480°C at the upper part of the sequence. As the depth of kerogen becomes deeper, the starting and maximum-release temperatures shifted toward higher, making the release peak narrower. The apparent shift of the temperatures was likely due to the earlier loss of compounds bonding to kerogen with lower activation energies.

To determine values of kinetic parameters for individual organic compounds on the release from kerogen, five kerogen samples of different burial depth from Neogene Shinjo sediments were heated in TG from room temperature to 800°C at increasing rate of 5, 10, 20, 30 and 60 °C min^{-1}, and released compounds were analyzed by GC/MS and compound release profiles by MS.

The large peaks at about 500 °C on the compound release profiles of m/z 78, 86, 92, 94, 100, and 116 by the TG-MS analysis were found and they were of benzene, hexane, toluene, phenol, heptane, and indene released from kerogen, respectively. T_{max} of compounds released from kerogen samples shifted towards higher temperature with temperature increasing rate, and fell in a range between 424.6 °C (heptane at 5 °C min^{-1}) and 516.9 °C (indene at 60 °C min^{-1}). The plot of $1/T_{max}$ vs. ln $(Hr/(T_{max})^2)$ for each compound on release showed a reasonably straight line with a high correlation coefficiency. As a result of determination of the kinetic parameters of an individual compound on release from kerogens by the equation of Braun and Burnham (1987), it was found that the activation energies and pre-exponential factors fell in a range between 43.1 kcal/mol (indene) and 60.9 kcal/mol (phenol), and between 3.56 x 10^{10} s^{-1} (indene) and 1.21 x 10^{16} s^{-1} (phenol), respectively. The average values of these kinetic

parameters had decomposition rates in order of indene > benzene, toluene > phenol > hexane, heptane. Therefore, it was found that hexane and heptane were more strongly bound with kerogen matrix than benzene, toluene and indene.

A mathematical model for compound release from kerogen was made using activation energy and pre-exponential factor and thermal history parameters such as geothermal gradient and rate of sediment subsidence. The model was applied for the Neogene Shinjo sediments, using the activation energies and pre-exponential factors for six compounds, and the geothermal gradient and the rate of the sediment subsidence.

The depth profiles of differential release extents of benzene, hexane, toluene, phenol, heptane and indene from kerogen differed each other. Their maximum releases were found around 134°C for benzene, 159°C for hexane, 136°C for toluene, 143°C for phenol, 152°C for heptane and 121°C for indene. The concentrations of reported extractable aliphatic hydrocarbons in Shinjo sediments increased at deeper sediments than those of extractable aromatic ones, which coincide with the results obtained by the model. However, there is a depth difference between those by the model and the reported studies, the model showing the depth profiles deeper than the reported extractable compounds. This difference may be corrected by the consideration of catalytic effect of the sediment constituents, especially clay minerals, to the kinetic parameters for thermal decomposition of kerogen.

In this study, the kind and release-temperatures of compounds released from kerogen were found using TG-GC/MS and TG-MS methods, and it was indicated that these methods enable to determine activation energies and pre-exponential factors for individual compounds on release from kerogen. Furthermore, it was indicated that the release extents of individual compounds by kerogen diagenesis could be estimated by a

mathematical model using kinetic parameters and temperature and rate of subsidence for thermal history of sediments. These results provide useful information about organic geochemistry and theory of petroleum generation.

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