

Geochemical studies of organic components in sediments around seafloor hydrothermal systems

山中, 寿朗
九州大学理学研究科地球惑星科学専攻

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Chapter 5.

Hydrothermal petroleum generation at hydrothermal areas associated with arc-backarc system

5-1. Hydrothermal petroleum identified from Wakamiko Caldera, Kagoshima Bay

Hydrothermally altered sediment, had significant gasoline-like smell, were obtained from the bottom of Wakamiko Caldera (Yamanaka *et al.*, 1999). Experimental results are described below.

5-1-1. Hydrocarbons and biomarker maturity indices in Wakamiko Caldera, Kagoshima Bay

Alkane compositions of the three sediments and CPI are shown in Table 13. The CPI values of the normal alkanes (C₁₄~C₃₂) in D341, D344 and D345 samples were 0.94, 1.44 and 1.62 respectively. The TIC chromatograms of aliphatic fractions are shown in Fig. 29.

The samples from the caldera floor (D341) and from the top of the knoll (D344 and D345) show quite distinct patterns of normal hydrocarbon compositions. The chromatogram of the bitumen in the D341 sediment shows a large hump of unresolved complex mixture (UCM). The pattern of hydrocarbon composition of the D341 sediment are comparable with a typical crude oil. The hydrocarbons, however, were enriched in aromatic fractions rather than the crude oil and the hydrocarbon composition were comparable with hydrothermal petroleum reported from the Guaymas Basin and Escanaba Trough (Fig. 30). The major components of the bitumen in the D341 sediment are the aromatic compounds which composed of major polycyclic aromatic hydrocarbons (PAHs) and an aromatic/naphthenic UCM (Table 14 and Fig. 31). The unsubstituted pyrolytic origin PAHs such as pyrene, fluoranthene, benzopyrene, and benzoperylene were also detected. Some biomarkers such as the steranes and the triterpanes were almost mature (Fig. 32) and the maturation indices of the biomarkers were comparable with hydrothermal petroleum reported from hydrothermal fields in the Guaymas Basin and Escanaba Trough (Table 15). Triterpane and sterane mature

indies are based on maturation of organic matter, PAH mature indies are based on thermal cracking of alkyl-chains. The PAH mature indies of D341 petroleum are smaller than that of Guaymas and Escanaba petroleums. Some sterenes, which is immature biomarkers, were also detected. The ratio of the two C₂₇ pentacyclic triterpanes 17 α (H)-22,29,30-trisnorhopane (T_s) and 18 α (H)-22,29,30-trisnorhopane (T_m) which is known to be an indicator of maturity (Seifert and Moldowan, 1978), was 6.25 which signified a petroleum derived from particularly immature source rocks. The phenanthrene to methylphenanthrenes (P/MP) ratio and methylphenanthrene indices fall under the ranges of other hydrothermal petroleums (Kawka and Simoneit, 1990; Kvenvolden and Simoneit, 1990; Simoneit, 1994). The C₂₇~C₂₉ steranes composition in the caldera deposits indicates that the source organic matter for the petroleum is accumulated in bay environment (Fig. 33; Huang and Meinschein, 1979).

In contrast, the small amount of the bitumen extracted from the knoll deposits was composed mainly of asphaltic compounds containing hetero atoms such as nitrogen, sulfur, and oxygen. The aromatic fraction in the knoll deposits was minor and the individual pyrolytic PAHs were under detection limit. The TIC chromatogram of the aliphatic fraction in the knoll deposits (Fig. 29) showed a small hump of the UCM and some mono-unsaturated normal hydrocarbons can be distinguished. The bimodal distribution of the normal hydrocarbons suggests the organic sources are both of autochthonous and allochthonous origins. Many biomarkers in the knoll deposits were under detection limit, only immature isomers such as 5 α ,14 α ,17 α -cholestane (20R) and 5 α ,14 α ,17 α -ergostane (20R) were identified.

5-1-2. Carbon isotope ratios of light hydrocarbons in fumarolic gases and sulfur isotope ratios of hydrothermal minerals in Wakamiko Caldera

For clarify the origin of light hydrocarbones and sulfide in fumarolic gases of the Kagoshima Bay, gas compositions of the fumarolic gases and isotope compositions of carbon and sulfur were measured (Table 16). The gases are demonstrated to be derived from volcanic

activity, and the gas compositions are changing associated with volcanic activity (Oosaka *et al.*, 1992). The maximum gas temperature $>200^{\circ}\text{C}$ were observed (Oosaka, *et al.*, 1992), although measured temperature during "Dolphin 3K" dive in 1998 was approx. 40°C . The major component of the gas was carbon dioxide (77.7% by volume) and methane (9.7%), ethane (43ppm) and propane (12ppm) were minor component. $\delta^{13}\text{C}_{\text{PDB}}$ value of carbon dioxide was $-8 \pm 0.5 \text{‰}$. $\delta^{13}\text{C}_{\text{PDB}}$ value of methane was $-30 \pm 0.1 \text{‰}$.

A hardened sediment was obtained from the bottom of the Wakamiko Caldera. The sediment was altered by hydrothermal activity and black sulfides and yellow~orange arsenic sulfides were mineralized. Elemental sulfur was also extracted by organic solvents. Those sulfur isotope ratios were also measured (Table 16). The $\delta^{34}\text{S}$ values (4~6‰) were similar each other and were distinguished clearly from the values of the sulfide provided by sulfate reducing bacteria ($< 0\text{‰}$ relative to CDT: Thode, 1988).

5-1-3. Organic geochemical features of petroleum-like hydrocarbons yielded from Wakamiko Caldera

Table 15 shows maturation indices of sterane and triterpane biomarkers in the caldera are as high as the Guaymas and Escanaba hydrothermal petroleums by Kvenvolden and Simoneit (1990) and Simoneit (1994). These maturity levels of the hydrocarbons from the Wakamiko Caldera are slightly lower than those of the Tertiary crude oil in the Niigata sedimentary basin, Japan by Sakata *et al.* (1988). The P/MP ratio indicates the alteration of the organic matter at $<300^{\circ}\text{C}$ (Ishiwatari and Fukushima, 1979). The other PAH mature indices are lower than the other hydrothermal petroleum, indicating that generation temperature of the caldera hydrocarbons is lower than them. The pyrolytic PAHs, however, are made at high temperatures in excess of 300°C (Kawka and Simoneit, 1990). The various indices of maturation in the caldera hydrocarbons suggests the mixing of the hydrocarbons in several maturation stages, and significant content of pyrolytic PAHs indicates pyrolytic formation of the oil from immature kerogens rather than simple diagenesis. These geochemical features

indicate that the petroleum-like hydrocarbons in the caldera deposits are typical hydrothermal petroleum.

Organic geochemistry of the sediments from the knoll top indicate that bitumen is unaltered by hydrothermal activities. CPI values of aliphatic hydrocarbons in D344 and D345 sediments was very small, although it must be attributed to fossil fuel pollution through water column. It is important to notice that well altered hydrothermal petroleum was identified only in the caldera floor sample. Hydrothermal petroleum of the caldera is likely not migrate from the deeper beneath the caldera but to originate within the sediment deposited on the caldera floor. Very thin sediment cover on the knoll top must be attributed no significant petroleum generation.

Table 13 Alkane compositions of the sediment samples in the Wakamiko Caldera and on the knoll, Kagoshima Bay

Carbon number	D341 $\mu\text{g/g}$	D344 $\mu\text{g/g}$	D345 $\mu\text{g/g}$
13	0.297	0.047	0.005
14	2.795	0.209	0.029
15	12.479	0.239	0.070
16	9.589	0.505	0.090
17	8.692	0.510	0.095
18	18.836	0.411	0.108
19	18.035	0.435	0.101
20	14.325	0.160	0.052
21	9.689	0.138	0.042
22	10.432	0.086	0.040
23	7.067	0.319	0.053
24	4.072	0.223	0.077
25	3.105	0.405	0.097
26	2.813	0.136	0.065
27	1.920	0.191	0.130
28	3.655	0.037	0.064
29	0.459	0.116	0.176
30	0.342	0.011	0.051
31	0.221	0.060	0.137
32	0.129	0.017	0.007
33	0.110	0.010	0.013
Total n-alkane	129.062	4.262	1.503
Pristane	70.711	0.579	0.117
Phytane	57.417	0.591	0.035
CPI	0.94	1.43	1.59
Pr/Ph	1.23	0.98	3.33

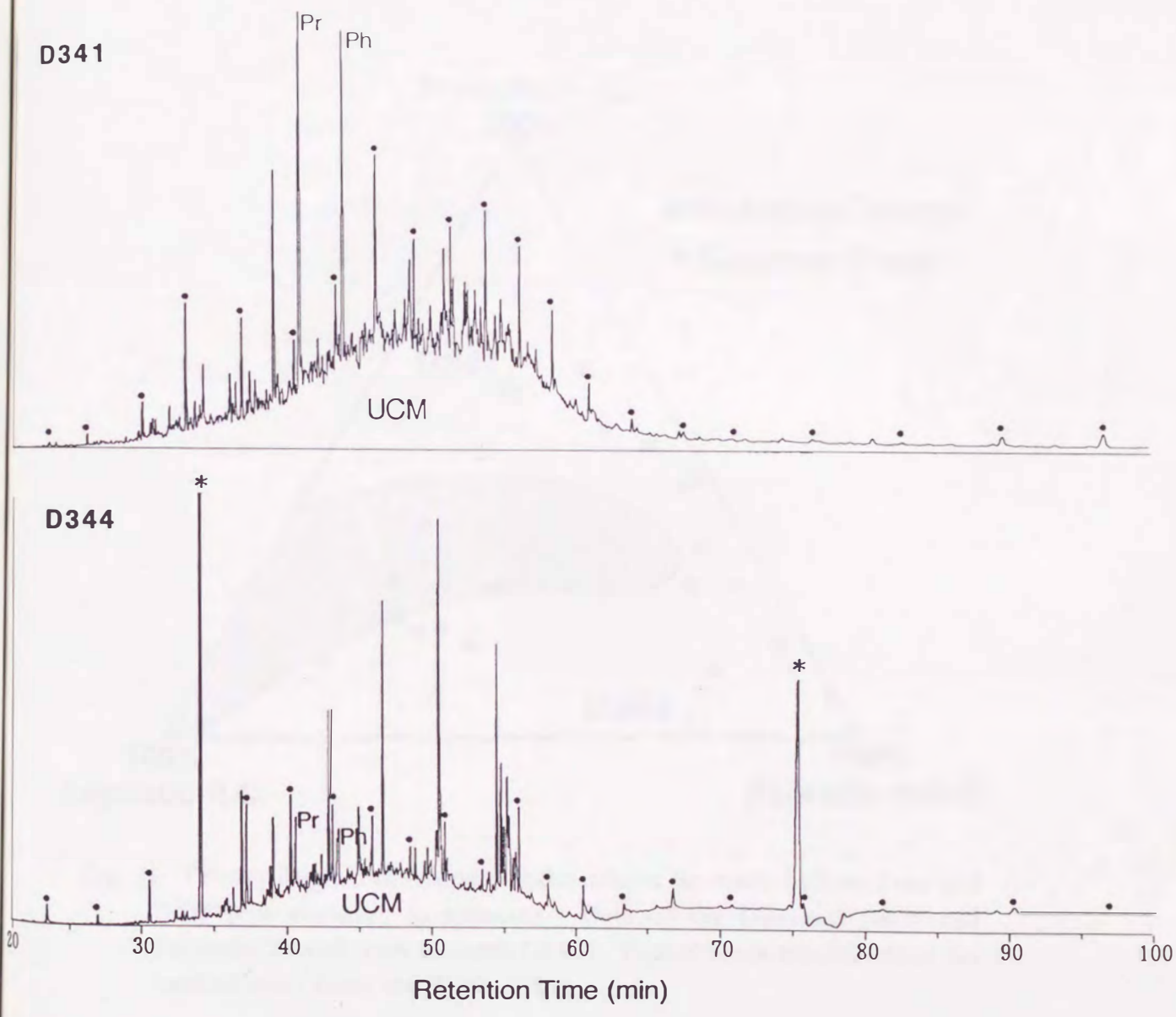


Fig. 29 TIC chromatograms of the aliphatic fractions in Samples D341 and D344 obtained from the northern part of Kagoshima Bay.

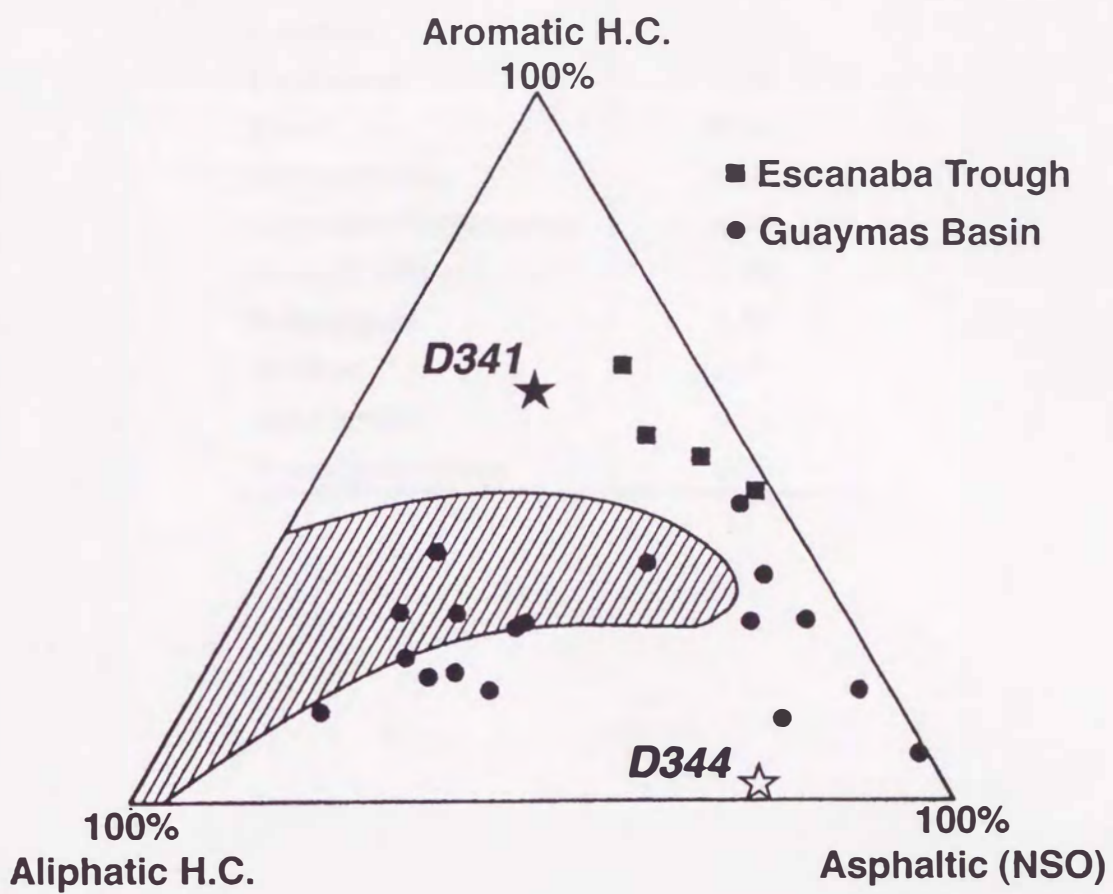


Fig. 30 Ternary diagram of saturated hydrocarbons, aromatic hydrocarbons and NSO plus asphaltic components. Data of the Guaymas Basin and Escanaba Trough from Simoneit (1993). Typical crude oils fall within the hatched area (Tissot and Welte, 1984).

Table 14 Major PAHs in the bottom sediment sample of the Wakamiko Caldera

Major PAHs	D341 μg/g dry sediment
Methylnaphtharene	6.63
Dimethylnaphtharene	7.63
Fluorene	0.38
Phenanthrene	20.54
Methylphenanthrene	82.09
Antracene	15.73
Fluorantene	3.53
Pyrene	40.65
Benzoantracene	5.39
Chrysene(+Triphenylene)	6.74
Benzo(b, k)fluorantene	1.66
Benzopyrene	2.53
Perylene	2.06
Indenopyrene	0.19
Benzo(ghi)perylene	0.57

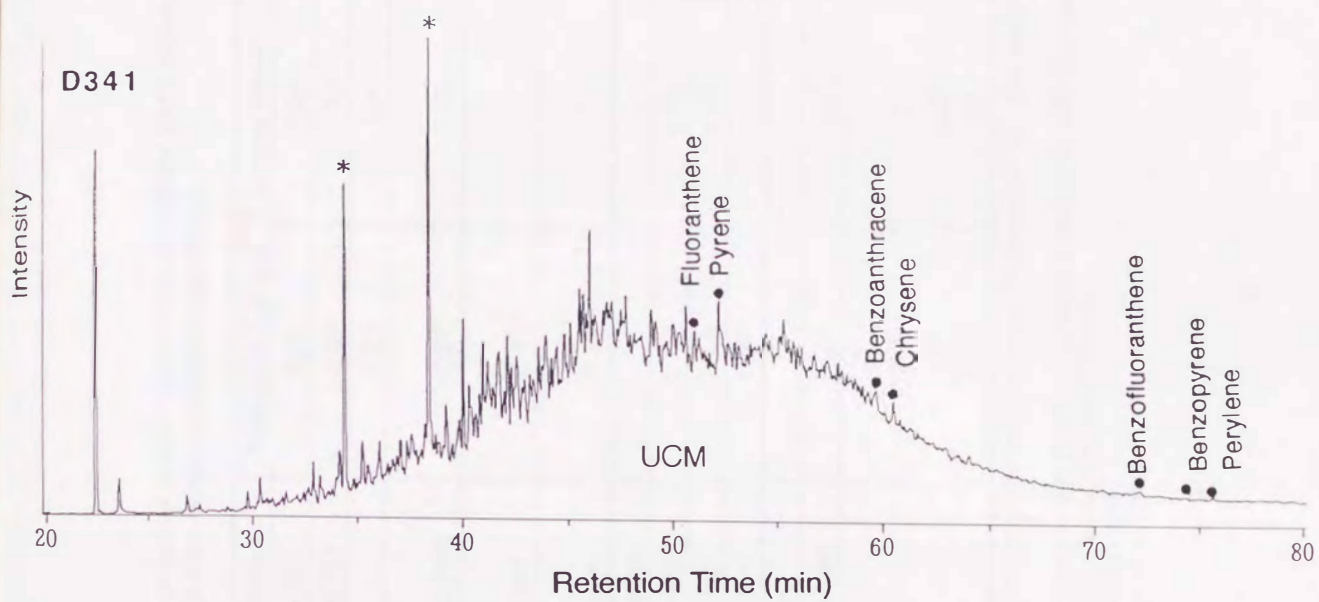


Fig. 31 TIC chromatogram of the aromatic fraction in Sample D341 from the Wakamiko Caldera. Rabeled peaks are major PAHs.

Table 15 Comparison of the molecular mature indices of biomarkers and PAHs between the Wakamiko Caldera (D341) and other hydrothermal areas bearing hydrothermal petroleum

Triterpane mature biomarker	Wakamiko Caldera	Guaymas Basin*	Escanaba Trough**
C32 hopane 22S/(22S+22R)	0.53	0.57	0.42
C31 hopane 22S/(22S+22R)	0.59	0.53	0.46
T_w/T_s	6.25	6.4	27
C30 Hopane 17 β (H),21 α (H)/17 α (H),21 β (H)	0.21	0.29	0.63
C31 Hopane (22R+22S)/C30 $\alpha\beta$ Hopane	0.62		
C32 Hopane (22R+22S)/C30 $\alpha\beta$ Hopane	0.33		
Sterane mature biomarker			
C27 diasterane 20S(20S+20R)	0.50	0.62	0.53
C29 sterane 20S(20S+20R)	0.43	0.28	0.13
C21~29 sterane L/(L+H)***	0.27		
PAH mature indices			
Phenanthrene/Methylphenanthrenes	0.25	0.57	3.33
Methylphenanthrene index			
MPI1†	0.75	1	0.39
MPI2†	0.71	1.25	0.41
MPI3††	0.72	1.5	

*Data from Kvenvolden and Simoeit (1990) and Kawka and Simoneit (1994). The sample was collected by DSV *Alvin*, dive 1172.

**Data from Kvenvolden and Simoeit (1990). The sample was collected by DSV *Sea Cliff*, dive 659.

*** 5 α -sterane (C21+C22)/(C21+C22+C27+C28+C29) ratio

†Ratios, as defined by Radke et al. (1982)

††Ratio, as defined by Garrigues et al. (1988)

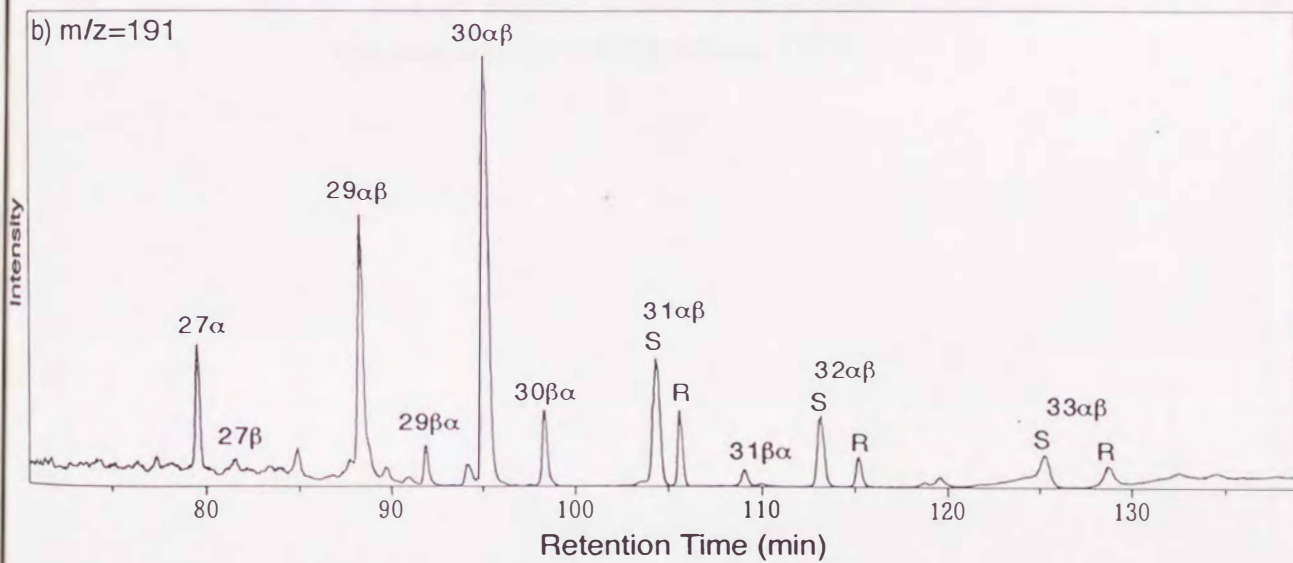
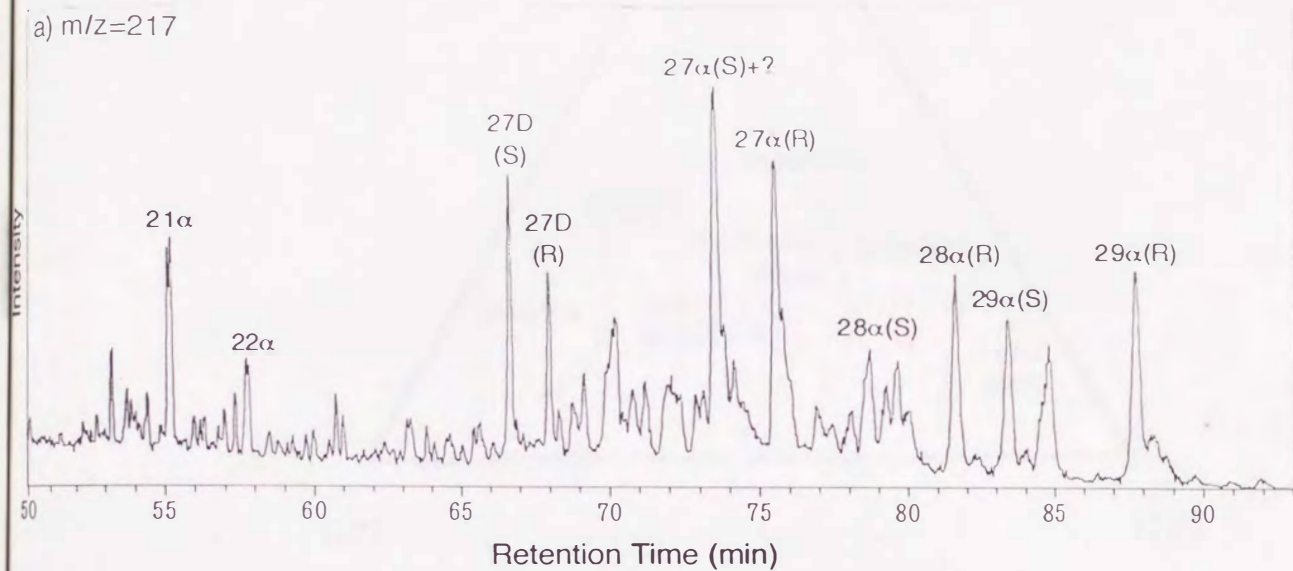


Fig. 32 Mass fragmentgram of biomarker steranes and triterpanes in Sample D341 from the Wakamiko Caldera.

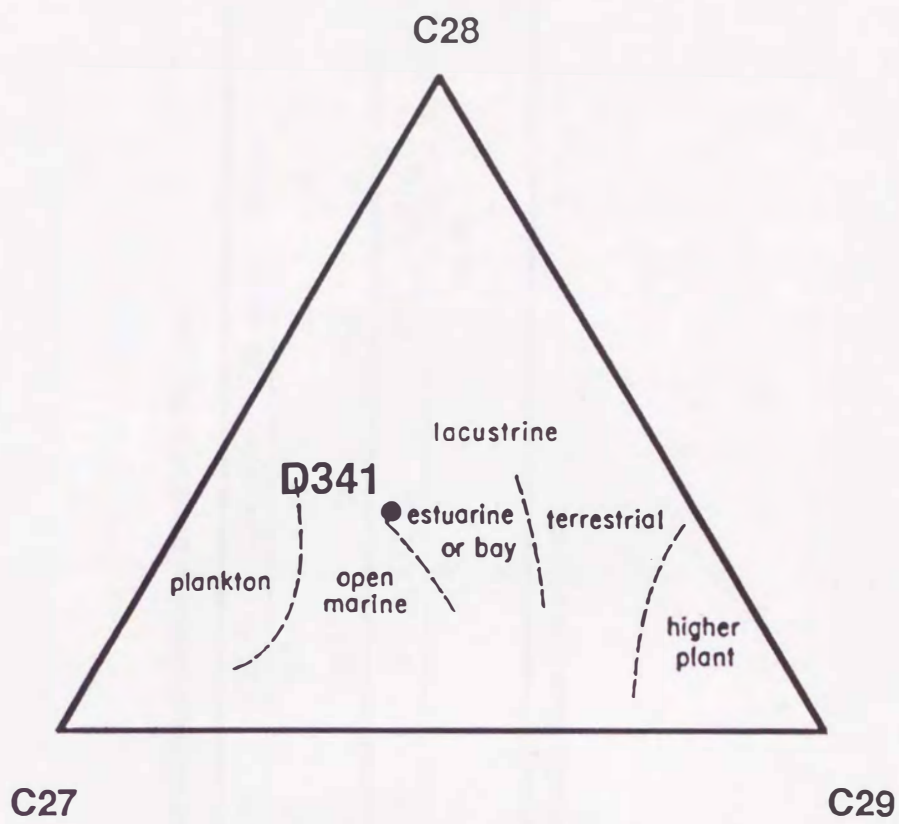


Fig. 33 Ternary diagram of Biomarker sterane compositions (C_{27-29}) as source indicator (Huang and Meinschein, 1979).

Table 16 Fumarolic gas compositions and isotope compositions of carbon and sulfur in the gases

Site	CO ₂ %	O ₂ %	N ₂ %	Ar %	CH ₄ %	C ₂ H ₆ ppm	C ₃ H ₈ ppm	He ppm	H ₂ ppm
Caldera	77.7	1.2	7.1	0.23	9.7	43	12	4.2	4.1
Knoll	68.9	1.7	10.5	0.19	18.7	55	6.6	4.3	347
Site	$\delta^{13}\text{C}_{\text{PDB}}$ methane ‰	$\delta\text{D}_{\text{SMOW}}$ methane ‰	$\delta^{13}\text{C}_{\text{PDB}}$ CO ₂ ‰	$\delta^{34}\text{S}_{\text{CDT}}$ H ₂ S ‰	C1/(C2+C3)*				
Caldera	-30.28	-160.3	-8.52	+6.49	874.9				
Knoll	-28.91	-166.7	-7.85		1001.2				

*C1/(C2+C3)=ratio of the cocentrations of methane to sum of ethane and propane

5-2. Hydrocarbon distributions in the sediments of the other hydrothermal areas

5-2-1. Hydrocarbons in DESMOS caldera

Remarkable amount of hydrocarbons are detected from both sediment samples (Table 17). The TIC chromatograms are shown in Fig. 34. Distribution patterns of n-alkanes show monomodal (maximum at C₂₅) and no carbon number preference, which are similar to that of conventional crude oil. The CPI values of D916 and D921 sediments are 1.45 and 1.02, respectively. Small hump of the background, UCM, are also shown in also both TIC chromatograms of aliphatic fractions. Similar aromatic hydrocarbons are detected in both samples. Especially, poly aromatic hydrocarbons (PAHs) are major components of aromatic fractions of both samples (Table 18). The concentrations of the PAHs are very low ($\leq 0.16 \mu\text{g/g}$ dry sediment), and highly polycyclic aromatics could not be identified. The pyrolytic origin PAHs such as pyrene and fluoranthene were detected.

5-2-2. Hydrocarbons at the North Knoll of Iheya Ridge

Abundance of normal and other remarkable hydrocarbons in Sample D1030 were shown in Table 19 and Fig. 35. Total concentration of normal alkanes in Sample D1030 was $4.56 \mu\text{g/g}$ dry sediment. CPI value of normal alkanes (C₁₄~C₃₂) in Sample D1030 was 2.1. Long chain alkanes were abundant in Sample D1030 and remarkable odd carbon number preference could be seen. CPI value of the alkanes longer than C₂₄ was 4.1, indicating typical terrigenous input. Small hump of UCM of TIC chromatogram could be seen at the range of short chain alkanes (C₁₆~C₂₆). Hydrocarbon fractions of D857R and D857B sediments were not measured because sample amounts are not enough for analyses.

Some PAHs were identified in the aromatic fraction of D1030 sediment (Table 20). The peak of each PAHs on TIC chromatogram were quite low, therefore, their concentrations could not be calculated. Some alkylated naphthalene and phenanthrene were contained. The pyrolytic origin PAHs such as pyrene and benzoanthracene were also detected.

5-2-3. Hydrocarbons in Myojin Caldera

Normal alkanes were identified ranging from C₁₅ to C₃₂ by GC/MS. Total concentrations of n-alkanes in D1008 and D1011 sediments were 4 and 4.8 μg/g dry sediment, respectively (Table 21 and Fig. 36). The CPI values of the both sediments were almost 1. Pristane and phytane, and also other isoprenoid type hydrocarbons were detected. The pristane/phytane ratios were 0.33 and 0.97, indicating sedimentation under anoxic condition. While the concentrations of the aliphatics was quite low, the small hump of the background of UCM were confirmed from the mass fragmentgram of M/Z=57, which is a major fragment of alkanes. Those features strongly suggest that hydrocarbons originated from matured oil, although it is difficult to exclude possibility of fossil fuel pollution or hydrothermal alteration. Absence of long chain alkanes (>C₂₆) in D1011 sediment indicates dominant input of terrigenous material, although this is not accordance with the fatty acid composition.

While concentrations of aromatic fraction were very low, some PAHs were detected. All the detected PAHs were listed in Table 22. Methyl phenanthrenes were major components of PAHs. Pyrene and fluoranthene of pyrolytic origin were also detected. The other higher molecular weight PAHs were under detection limit.

Table 17 Alkane compositions in the sediment samples of the DESMOS Caldera, Manus Basin

Carbon number	D916 $\mu\text{g/g}$	D921 $\mu\text{g/g}$
16	0.066	0.020
17	0.182	0.046
18	0.436	0.034
19	0.614	0.029
20	0.098	0.025
21	0.296	0.056
22	0.410	0.089
23	0.335	0.243
24	0.592	0.277
25	0.814	0.246
26	0.406	0.342
27	0.397	0.817
28	0.291	0.461
29	0.256	0.382
30	0.134	0.609
31	0.132	0.226
32	0.064	0.048
33	0.016	0.075
Total n-alkane	5.541	4.024
Pristane	0.028	0.016
Phytane	0.109	0.017
CPI ₂₄₋₃₂	1.45	1.07
Pr/Ph	0.25	0.98

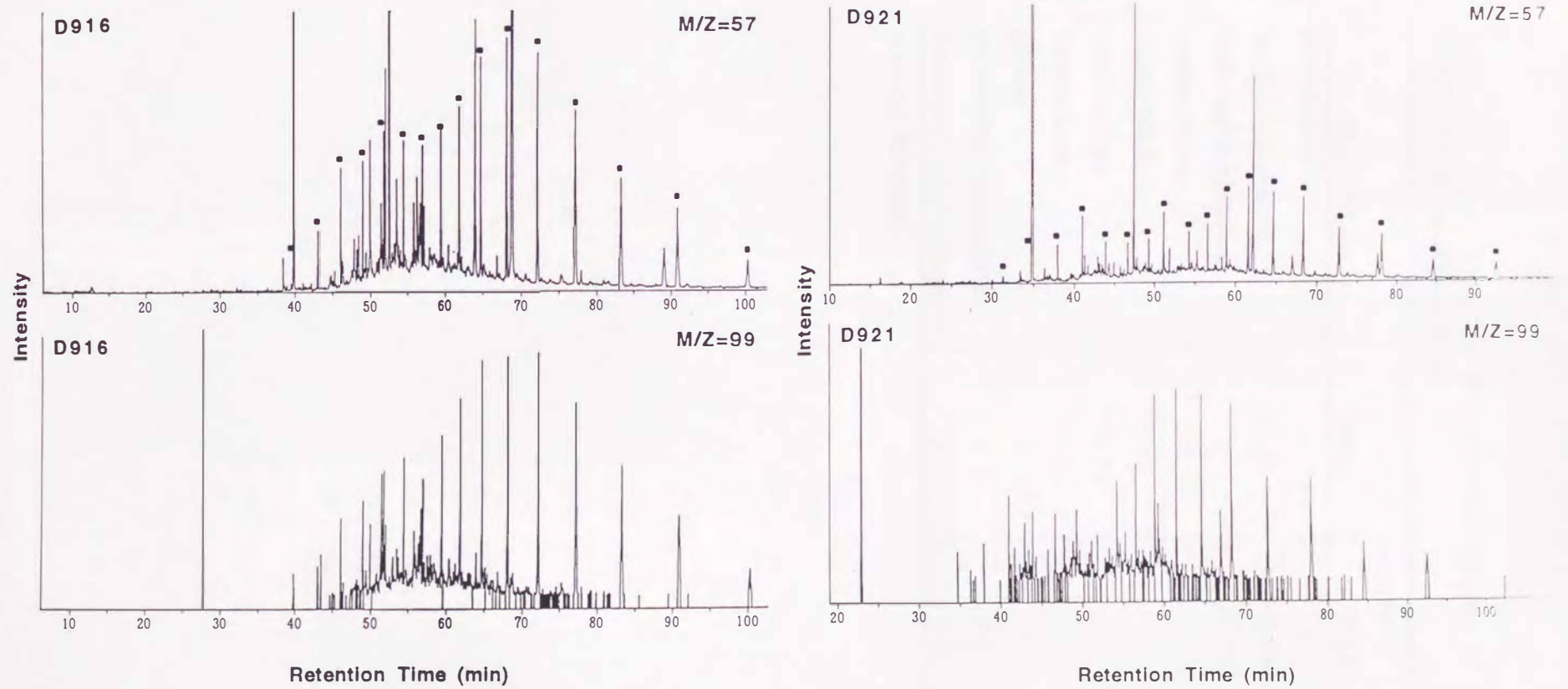


Fig. 34 Mass fragmentgrams ($M/Z=57$ and 99) of the aliphatic fractions in Samples D916 and D921 obtained from the DESMOS Caldera, Manus Basin.

Table 18 Major PAHs in the sediment samples of the DESMOS Caldera, Manus Basin

Major PAHs	ng/g dry sediments	
	D916	D921
Naphthalene	+	+
methyl-naphthalene	40.60	18.20
Dimethyl-naphthalene	+	20.26
Acenaphthene	n.d.	+
acenaphthalene	5.92	+
phenanthrene	158.57	+
fluoranthene	+	+
pyrene	+	+
tetramethyl-phenanthrene	+	n.d.
Benzoanthracene+Chrysene	+	n.d.

n.d., not detection

Table 19 Alkane compositions in the sediment of the North Knoll, Iheya Ridge

D1030	
Carbon number	$\mu\text{g/g}$ dry sediment
13	0.002
14	0.004
15	0.023
16	0.088
17	0.193
18	0.222
19	0.207
20	0.212
21	0.249
22	0.271
23	0.365
24	0.260
25	0.421
26	0.197
27	0.499
28	0.138
29	0.681
30	0.051
31	0.422
32	0.014
33	0.040
Total n-alkane	4.558
Pristane	0.153
Phytane	0.086
CPI ₁₄₋₃₂	2.11
CPI ₂₄₋₃₃	4.14
Pr/Ph	1.78

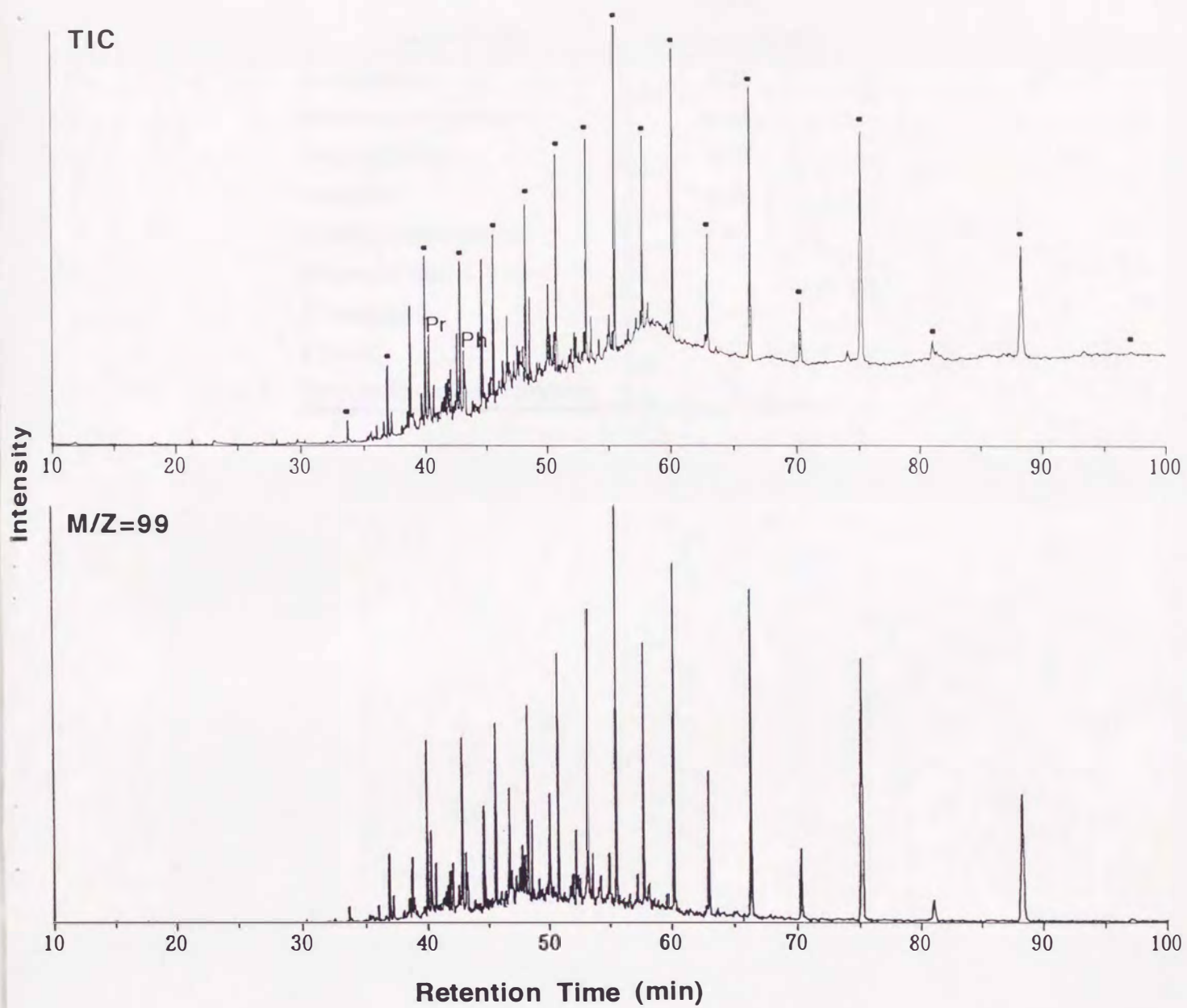


Fig. 35 TIC chromatogram of aliphatic fraction of Sample D1030 obtained from the North Knoll of Iheya Ridge, Okinawa Trough.

Table 20 Major PAHs in the sediment sample of the North Knoll, Iheya Ridge

Major PAHs	D1030 ng/g dry sediment
Naphthalene	2.26
Methyl-naphthalene	41.62
Acenaphthene	5.53
Fluorene	8.20
Methyl-phenanthrene	+
Dimethyl-phenanthrene	+
Fluoranthene	+
Pyrene	+
Benzoanthracene+Chrysene	+

Table 21 Alkane compositions in the sediment samples of the Myojin Caldera, Izu-Ogasawara Arc

Carbon number	D1008 $\mu\text{g/g}$	D1011 $\mu\text{g/g}$
15	0.059	
16	0.191	0.073
17	0.381	0.188
18	0.522	0.261
19	0.438	0.363
20	0.582	0.346
21	0.464	0.342
22	0.387	0.314
23	0.271	0.329
24	0.197	0.309
25	0.304	0.379
26	0.244	0.463
27		0.443
28		0.339
29		0.338
30		0.141
31		0.102
32		0.055
Total n-alkane	4.040	4.785
pristane	0.157	0.066
phytane	0.478	0.068
CPI	0.98	1.11
Pr/Ph	0.33	0.97

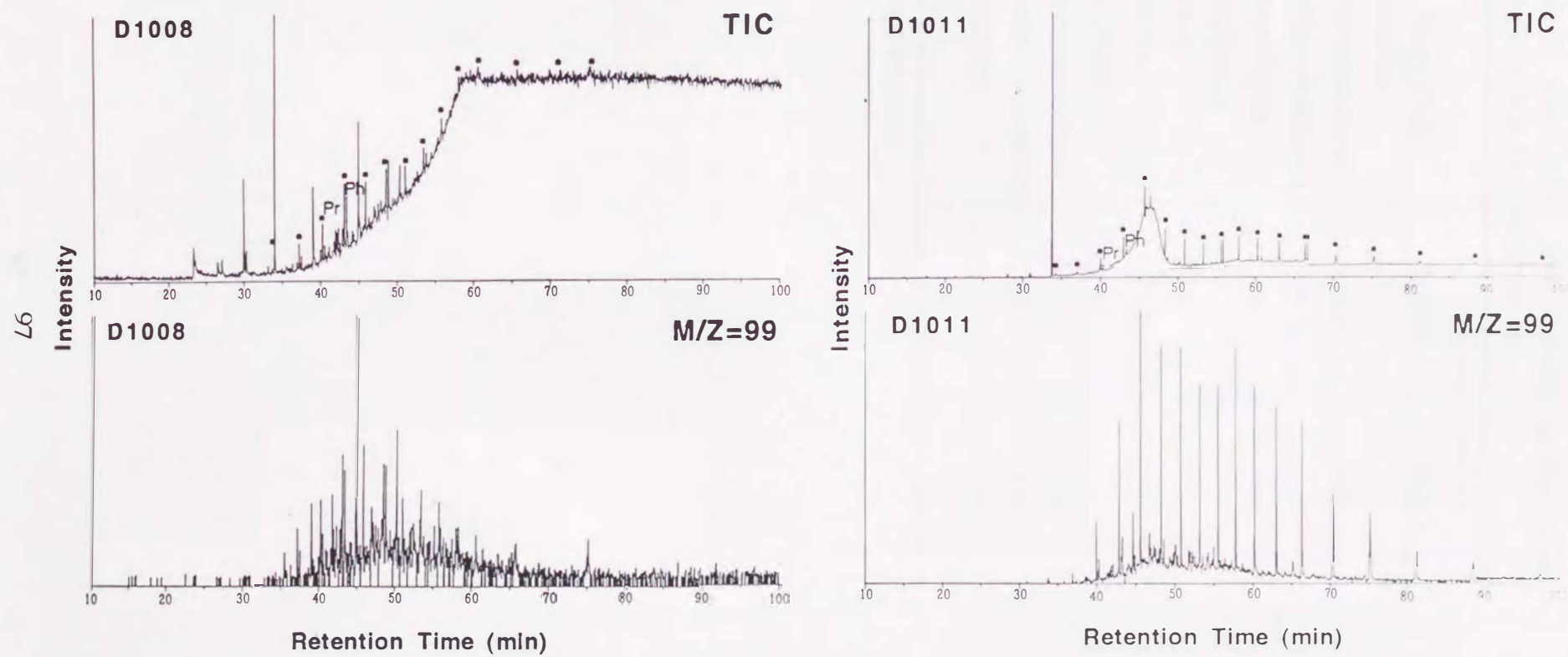


Fig. 36 TIC chromatograms and mass fragmentgrams of aliphatic fractions in Samples D1008 and D1011.

Table 22 Major PAHs in the sediment samples of the Myojin Caldera, Izu-Ogasawara Arc

Major PAHs	ng/g dry sediment	
	D1008	D1011
Naphthalene	+	+
Methyl-naphthalene	55.25	215.03
Dimethyl-naphthalene	24.46	+
Acenaphthylene	+	n.d.
Acenaphthene	+	+
Fluorene	+	+
Anthracene	+	+
Phenanthrene	+	+
Methyl-phenanthrene	+	+
Dimethyl-phenanthrene	n.d.	n.d.
Fluoranthene	+	+
Pyrene	+	+

n.d., not detection

5-3. Discussion

5-3-1. Distributions of petroleum-like hydrocarbons at the hydrothermal areas

The aliphatics characterized by no carbon number preference and presence of UCM were found at the three hydrothermal areas, Kagoshima Bay, DESMOS Caldera and Myojin Caldera. Those three hydrothermal areas are located at submarine calderas. Especially, the sediments obtained from the bottom of the Wakamiko Caldera, as described above, contained significant amount of hydrothermal petroleum. The D1030 sediment obtained from Okinawa Trough contained many aliphatics including many alkenes characterized higher CPI value (>2). The normal saturated hydrocarbons were enriched in long chain hydrocarbons ($>C_{24}$) and show a distinct even carbon number preference ($CPI_{24-33}=4.1$), indicating large input of terrigenous matters. The fatty acid composition of the D1030 sediment shows similar distribution such as low L/H ratio.

The experimental results suggest that the petroleum-like hydrocarbons in the Wakamiko Caldera must be hydrothermal origin. The concentration of hydrocarbons is quite high and the bitumen is enrichment in aromatic fractions (Fig. 30). The aromatic fractions are contained remarkable amounts of pyrolytic PAHs such as pyrene, fluoranthene, benzopyrene, and benzoperylene. The detailed geochemical features are described above. From the seismic profiles a magma chamber is recognized below the Wakamiko Caldera (Ono *et al.*, 1978; Takahashi, 1997). The magma is expected the heat source for hydrothermal activities. Significantly high helium isotope ratio ($^3\text{He}/^4\text{He}=9.5\times 10^{-6}$) and carbon isotope ratios of CO_2 ($\delta^{13}\text{C}_{\text{PDB}} = -7.58 \sim -8.52\%$) of fumarolic gases support this suggestion.

The small amounts of petroleum-like hydrocarbons were also found in the DESMOS Caldera and Myojin Caldera. The concentrations of those hydrocarbons are remarkable lower than that of the Wakamiko Caldera. The aromatic fractions contain small amounts of low-molecular weight PAHs. As indicated by Youngblood and Blumer (1975), presence of pyrolytic PAHs is interpreted as pyrolysate derived from air fall materials of oil and coal combustion in many case. However, both DESMOS Caldera and Myojin Caldera are located

at a distance of several hundred kilometers from land. The PAHs detected in these samples must be attributed to evidence for hydrothermal petroleum generation. It is notable that Sample D1011 from the Myojin Caldera show enrichment in long chain alkanes, which is not agreement with proportions of fatty acids which low content of long chain fatty acids and preference even to odd carbon number fatty acids. It suggests that the source of the hydrocarbons and fatty acids are different, the long chain alkanes are not terrigenous origin. The fatty acid compositions are considered to reflect just present ecosystem, so, the hydrocarbons may be migrated from the subsurface deposits in the caldera. In contrast, the aliphatics of the sediments obtained from Iheya Ridge occur as small humps of UCM ranged from C₁₆ to C₂₆, suggesting presence of petroleum-like hydrocarbons. Some PAHs were also detected. While it is difficult to elucidate the origin of the UCM, the sediment containing terrigenous organic matter takes oil pollution. The diffusion of oil pollution is considered to use an example of Sagami Bay and discussed Chapter 4-4.

The petroleum-like hydrocarbons of possible hydrothermal origin are recognized in the sediments obtained from the hydrothermal areas. In the depression such as submarine caldera the sedimentation rate is generally higher than that of the surroundings. The dissolved oxygen levels of the bottom water in the caldera are expected to decrease easily. In fact, the bottom water of Wakamiko Caldera was changed into anoxic and acidic by fumarolic gases and fluids particularly during summer in which stratified water structure is developed. Those geological and oceanographical conditions are expected to enhance the preservation of sedimentary organic matters. The submarine caldera involving active hydrothermal venting is expected to provide a good place for hydrothermal petroleum generation.

5-3-2. Possible fossil model of the simultaneously generation of petroleum and sulfide ore deposits associated with arc-backarc tectonics

Two distinct parallel mineralized belts, Oil-belt and Kuroko-belt, are recognized in the Green Tuff region of northeast Japan in the Middle Miocene. Both belts were running along the back-arc basin (proto-Japan Sea)(Fig. 37; Kajiwara and Sasaki, 1987). PUMOS hypothesis was purposed common source of these oil and sulfide ore deposits based on the oil and the sulfide ores that have the same range of sulfur and strontium isotope compositions (Kajiwara and Sasaki, 1987; Nakano *et al.*, 1989), although others had paid little attention to possible genetic links. Those parallel distributions were interpreted as a result of the differences for the required preservation factor between petroleum and sulfide ore minerals such as sedimentation rate and redox condition. This hypothesis has not been recognized the Kuroko ore deposits derived from hydrothermal fluids. However, discovery from the Wakamiko Caldera suggest that the genetic link between the petroleum and the Kuroko ore deposits can be interpreted by hydrothermal activity at sedimented caldera floor instead of PUMOS.

The light natural hydrocarbons in the Green Tuff reservoirs are also characterized by higher $\delta^{13}\text{C}$ and δD values. Fig. 38 are summarized the carbon and hydrogen isotope ratios of methane in the fumarolic gases and the Green Tuff natural hydrocarbons. The both can be plotted in the closed area indicating the thermogenic origin of Bernard *et al.* (1976). Methane involving the Guaymas petroleum with high $\delta^{13}\text{C}$ values (-47~-40‰ relative to PDB) is also thermogenic origin (Simoneit *et al.*, 1988). The methane in the both natural gases of the Green Tuff reservoirs and the fumarolic gases of Kagoshima Bay are generated associated with igneous activities of arc-backarc systems.

The $\delta^{34}\text{S}$ values of the hydrogen sulfide obtained from the fumaroles in the caldera (+6~-7‰ relative to CDT, Nedachi *et al.*, 1997) and the sulfide minerals in the hardened sediments (+2~+4‰) are similar to the average values of Kuroko ore deposits (+4.0‰: Kajiwara and Sasaki, 1987). Those $\delta^{34}\text{S}$ values were summarized in Fig. 39. The

environmental similarities between the Kagoshima Bay and the Miocene Green Tuff region have been suggested (Kitazato, 1979). The Kuroko ore deposits of the northeast Japan were generated in the back-arc depression just behind of the volcanic front (Fujioka, 1983). It is also suggests that the formation of caldera play an important role for Kuroko formation (Ohmoto, 1978). This tectonic setting is compare with the Kagoshima Graben.

The Kuroko ore deposits are well known to have been generated by seafloor hydrothermal systems related to submarine volcanisms (e.g. Ohmoto, 1996). High helium isotope ratios ($^3\text{He}/^4\text{He}=6.90\sim 8.67\times 10^{-6}$; Wakita *et al.*, 1990) are reported from the natural gases in the Green Tuff volcanic rock reservoirs. The helium isotope ratio of the vent fluid characterized by high concentration of hydrocarbons in the Guaymas Basin ($^3\text{He}/^4\text{He}=6.95\times 10^{-6}$) is also as higher as that of 21°N East Pacific Rise ($^3\text{He}/^4\text{He}=7.8\times 10^{-6}$) (Lupton, 1983). The ratio of the fumarole in the caldera is also high ($^3\text{He}/^4\text{He}=9.5\times 10^{-6}$). The helium isotope ratios were plotted in Fig. 40.

The reservoirs of the Green tuff volcanic rocks are considered to improve the pore properties by hydrothermal alteration followed the felsic submarine volcanism (Yamada and Uchida, 1997). Then the petroleum generation is commenced by the hydrothermal heated in a shorter period of time than the maturation of organic matter during burial (Yamada and Uchida, 1997). Furthermore, the source rocks of the northeast Japanese oil fields are reported to contain significant amount of PAHs (Taguchi, 1968). The Green Tuff petroleum is most likely hydrothermal origin and preserved and accumulated in the geologic strata.

Geologic and topographic scales of the Wakamiko Caldera is quite smaller than the Green Tuff region. It seems difficult to compare with the discovery from the Wakamiko Caldera and the Green Tuff region. Comparable large scale formation of hydrothermal petroleum, however, has been already reported from the Guaymas Basin, Gulf of California (e.g. Simoneit *et al.*, 1988). It is not unreasonable to think that simultaneous generation of petroleum and sulfide deposits are cause of the parallel distribution of them in the Green Tuff region. If hydrothermal petroleum generation will be found in the Okinawa Trough, it become better

example for explanation of genetic links between oil-belt and Kuroko-belt in the Green Tuff region.

The Myojin Caldera and Manus Basin also recognize the formation of Kuroko-like sulfide ore deposits (Iizasa *et al.*, 1997; Binns and Scott, 1993), which enriched in Au and Ag, and the $\delta^{34}\text{S}$ values of sulfide deposits in the Myojin Caldera indicates fairly narrow range between +3.4~+4.8‰ (Iizasa *et al.*, 1997). Considering geology, submarine topography and tectonic settings, the Manus Basin and Izu-Ogasawara Ridge is similar with the northeast Japan arc during late Miocene (Fujioka, 1997). Those area are also expected the simultaneously formation of the both hydrothermal petroleum and sulfide ore deposits. The petroleum formation depends on the abundance of the sedimentary organic matters.

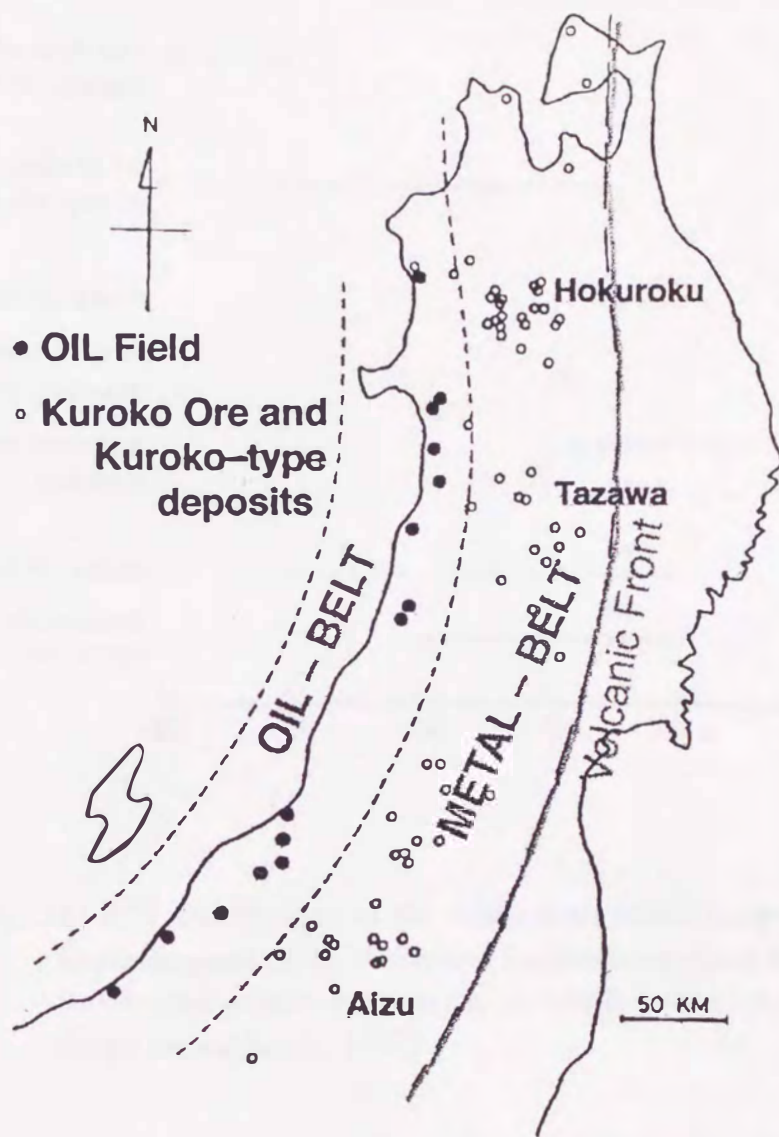


Fig. 37 Paired distribution of the metallic mineralization belt (Kuroko belt) and the oil-producing belt in the Neogene system of the northeast Japan (Kajiwara and Sasaki, 1987).

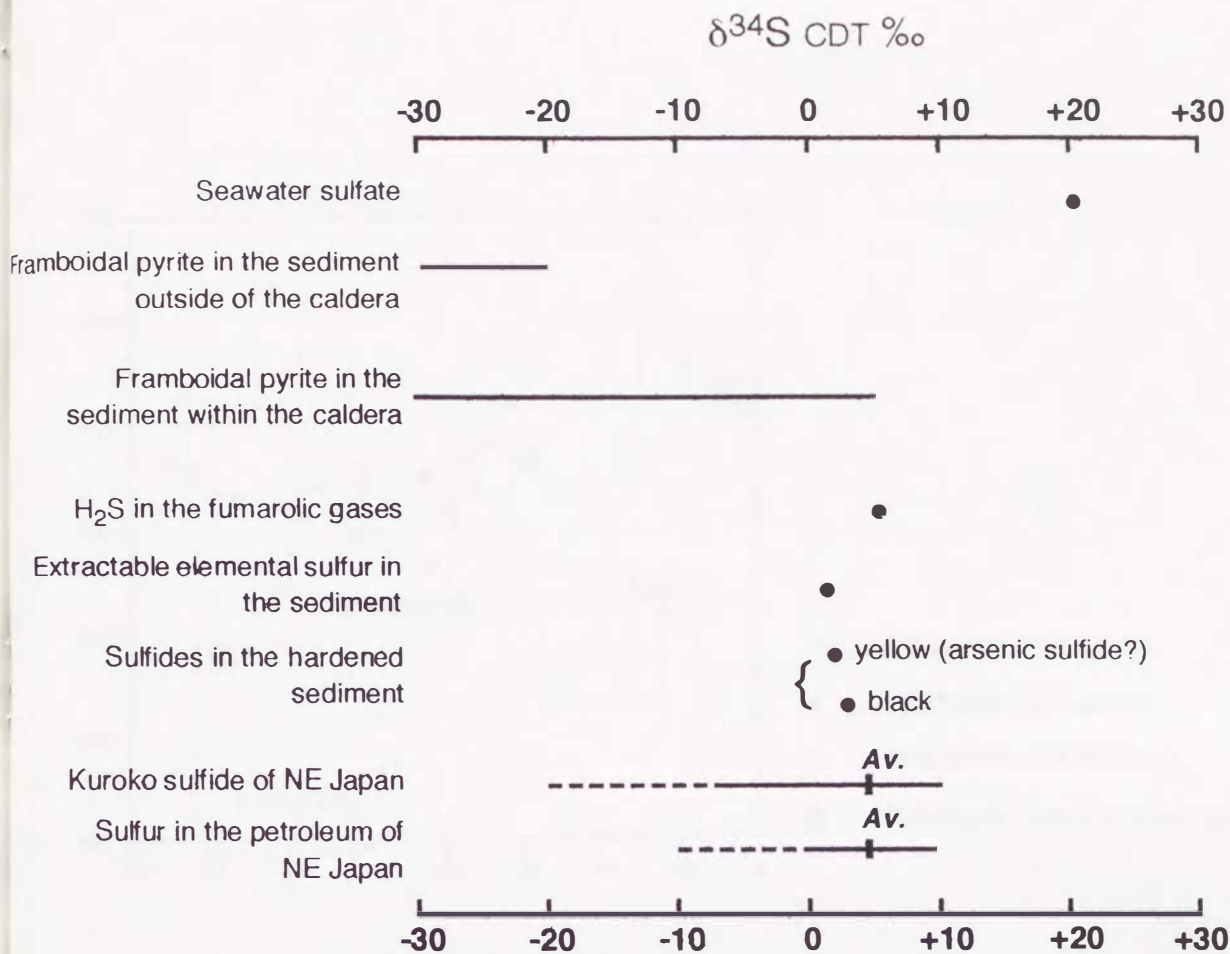


Fig. 38 $\delta^{34}\text{S}$ distributions of the sulfur compounds in the sediment and the fumarolic gases of the Wakamiko Caldera comparison with the Kuroko ore sulfides and organic sulfur in the petroleum yielded in the northeast Japan (Kajiwara and Sasaki, 1987).

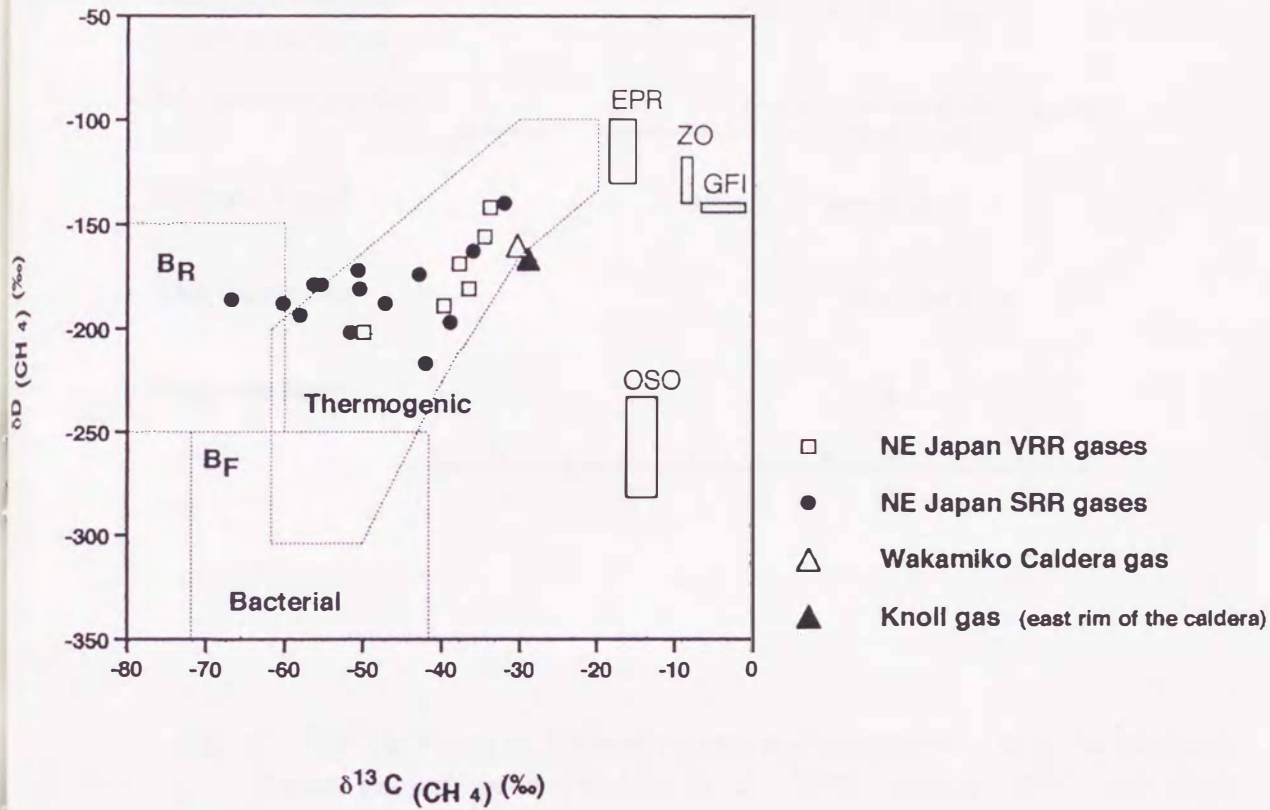


Fig. 39 Plot of δD vs. $\delta^{13}C$ of the methane in the fumarolic gases and natural gases of the northeast Japan (from Sakata, 1997). The boundary of bacteria and thermogenic methanes are drawn after Schoell (1988). The fields B_F and B_R are attributed to pathways of bacterial methanes from fermentation of acetate, and reduction of CO_2 , respectively. Area of four abiotic methanes are shown from comparison: EPR, geothermal methane from the East Pacific Rise; GFI, methane in fluid inclusions from alkalic igneous rocks, Greenland; ZO, methane issuing from the Zambales Ophiolite, Philippines; OSO, methane issuing from the Oman-Semail Ophiolite.

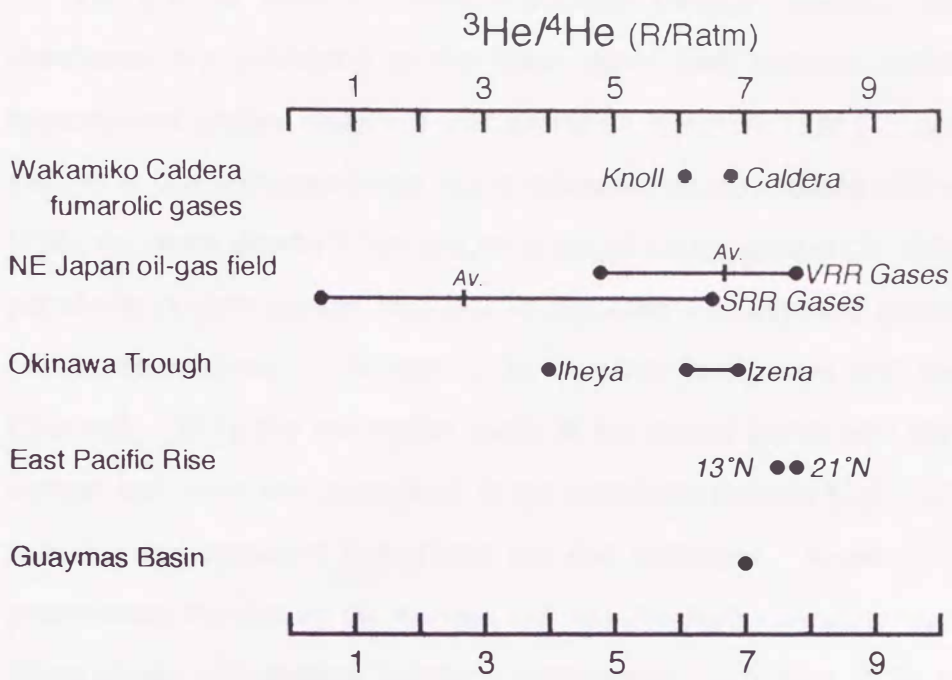


Fig. 40 $^3\text{He}/^4\text{He}$ ratios of fumarolic gases and comparisons with the northeast Japan naturel gases (Wakita et al., 1990; Sakata, 1997) and other hydrothermal systems (Lupton, 1983). SRR: sedimentary reservoir rock, VRR: volcanic reservoir rock.

5-4. Summary

The present discovery from Wakamiko Caldera indicates that the petroleum is simultaneously generated at the same space with massive sulfide deposits by the hydrothermal systems correlated with submarine volcanism. The petroleum of the Wakamiko Caldera is first discovered from active submarine volcano related with arc-backarc systems. While the water depth (200m) and thickness of source deposit (50~80m) of the occurrence petroleum is quite smaller than that of any other hydrothermal petroleum (>2000m and >300m, respectively, in the case of the Guaymas Basin) have been reported from seafloor (Simoneit, 1993), the maturation levels of the several biomarkers are almost equal. The sterane and triterpane biomarkers in the petroleum indicate high maturity, however, low maturity and immature biomarkers are also contained. Aromatic hydrocarbons are a predominant fraction of the bitumen and includes high concentrations of pyrolytic PAHs. Those organic geochemical features suggest pyrolytic formation of the petroleum rather than simple diagenesis. As Simoneit (1993) points out, hydrothermal alteration of organic matter is probably a ubiquitous process along the global rift systems and is a phenomenon that has been active over most of geologic time. Considerations of the similar spatial distribution and geochemical signatures of the petroleum and the Kuroko ore deposits in the Green Tuff region of the northeast Japan during Miocene may suggest their simultaneously generation by a common process such as a hydrothermal system found in the submarine Wakamiko Caldera. At the other submarine caldera occurred hydrothermal mineralization, such as DESMOS Caldera and Myojin Caldera, the hydrothermal petroleum generations are expected.

Chapter 6.

Conclusion

The fatty acid composition studies of sediment around hydrothermal areas revealed several notable characteristics commonly observed among the sediment-free hydrothermal systems, Myojin Knoll and Desmos Caldera. The most remarkable point is enrichment in monounsaturated fatty acids which are derived from aerobic bacterial metabolism. This is one of geochemical evidence for significant occurrence of bacterial chemosynthesis in hydrothermal areas. The second point is notable abundance of methyl-branched fatty acids derived from anaerobic bacteria. This suggests important contribution from bacterial alteration process in hydrothermal areas. The third point is depletion of PUFAs which are derived from a proxy of eukaryotic organisms. This indicates organic matter derived from sea surface production is overwhelmed by primary products of bacteria in seafloor hydrothermal areas. Together with significant high total fatty acid concentrations, the composition of these biomarker fatty acids indicate significantly high primary production of bacteria in hydrothermal areas.

In the sediment from Iheya Ridge, however, these hydrothermal characteristics are not obvious. Odd number preferred long chain fatty acids of terrigenous origin are dominant fatty acids in the sediment. This is accordance with high sedimentation rate around the Iheya Ridge caused by turbidite from the Asia continental shelf. The fatty acids specifically derived from bacterial metabolism associated with hydrothermal activities is overwhelmed by significant supply of terrigenous fatty acids. Although the Kagoshima Bay is surrounded by land, the sediment from the Wakamiko Caldera well show fatty acid composition characteristics of bacterial metabolism. In this area, thick sediment layer is mainly composed of volcanic ash and glasses and less terrigenous supply than the case of Okinawa Trough. The comparison of fatty acids composition between the Iheya Ridge and Kagoshima Bay provides an example for that sedimentation environment can easily conceal fingerprint

biomarkers related with hydrothermal activities.

The hydrocarbon composition study of sediment from the Wakamiko Caldera, Kagoshima Bay indicates significant hydrothermal petroleum formation. Present sediment at the caldera floor is considered as source rock, and high temperature fluids and/or fumarolic gases circulated within sediment layer is considered as heat source. Together with the occurrence of Kuroko-like sulfide in the same space, close relationship of formation of petroleum and sulfide ore are demonstrated. This would provide an important clue for interpretation of genetic links between the oil-belt and the Kuroko-belt observed in the Green Tuff region of Tertiary northeast Japan.

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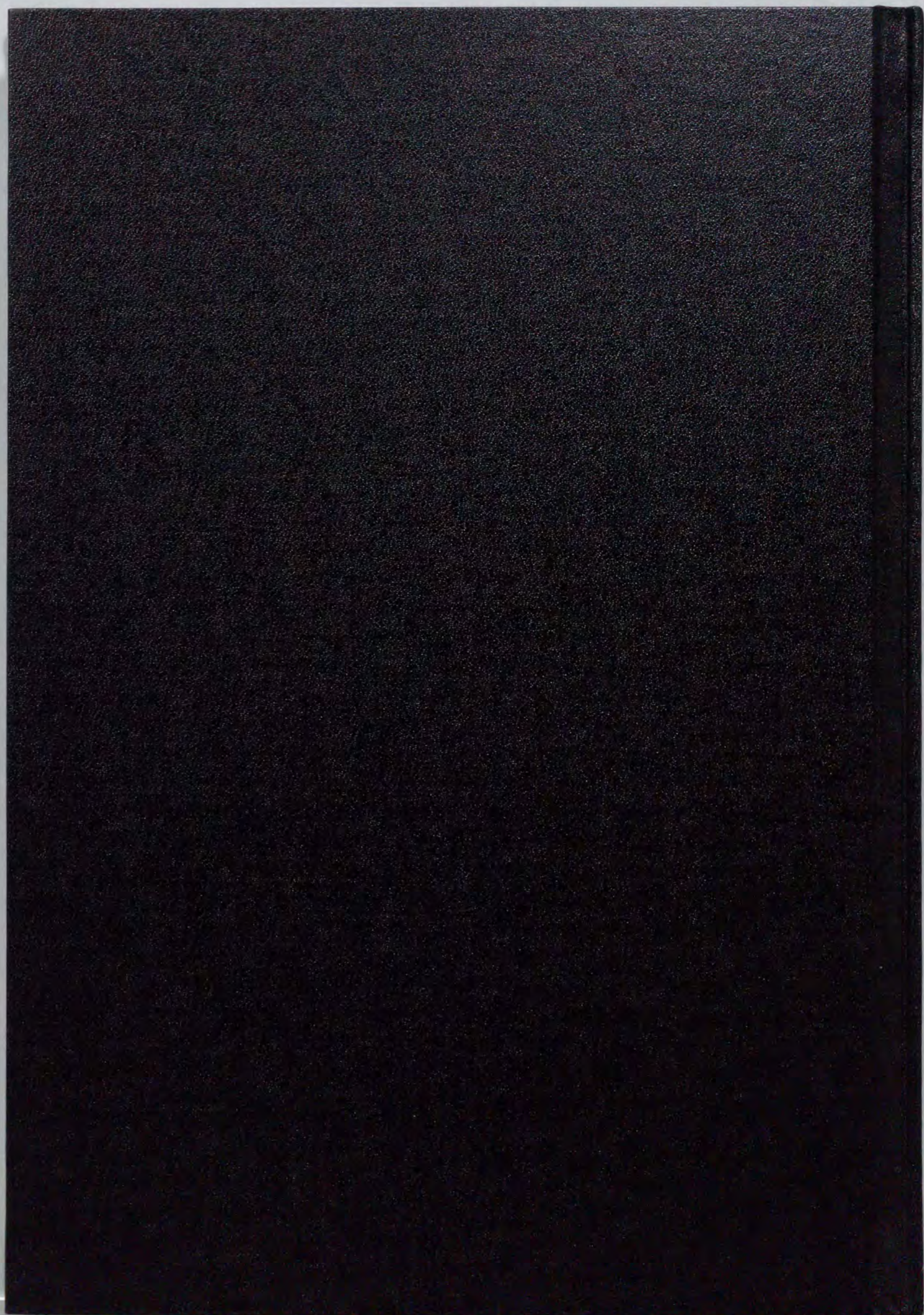
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