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Geochemical studies of organic components in sediments around seafloor hydrothermal systems

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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 indies 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 (C_{14}~C_{32}) 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 indies of the biomarkers were comparable with hydrothermal petroleums 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 craking 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 C_{27} pentacyclic triterpanes 17α(H)-22,29,30-trisnorhopane (T_s) and 18α(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 C_{27}~C_{29} 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 5α,14α,17α-cholestane (20R) and 5α,14α,17α-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°C were obsereved (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 were minor component. $\delta^{13}C_{PDB}$ value of carbon dioxide was -8 ± 0.5 ‰. $\delta^{13}C_{PDB}$ value of methane was -30 ± 0.1 ‰.

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 $\delta^{34}S$ values (4~6‰) were similar each other and were distinguished clearly from the values of the sulfide provided by sulfate reducing bacteria (< 0‰ 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°C (Ishiwatari and Fukushima, 1979). The other PAH mature indies 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 μg/g	D344 μg/g	D345 μg/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

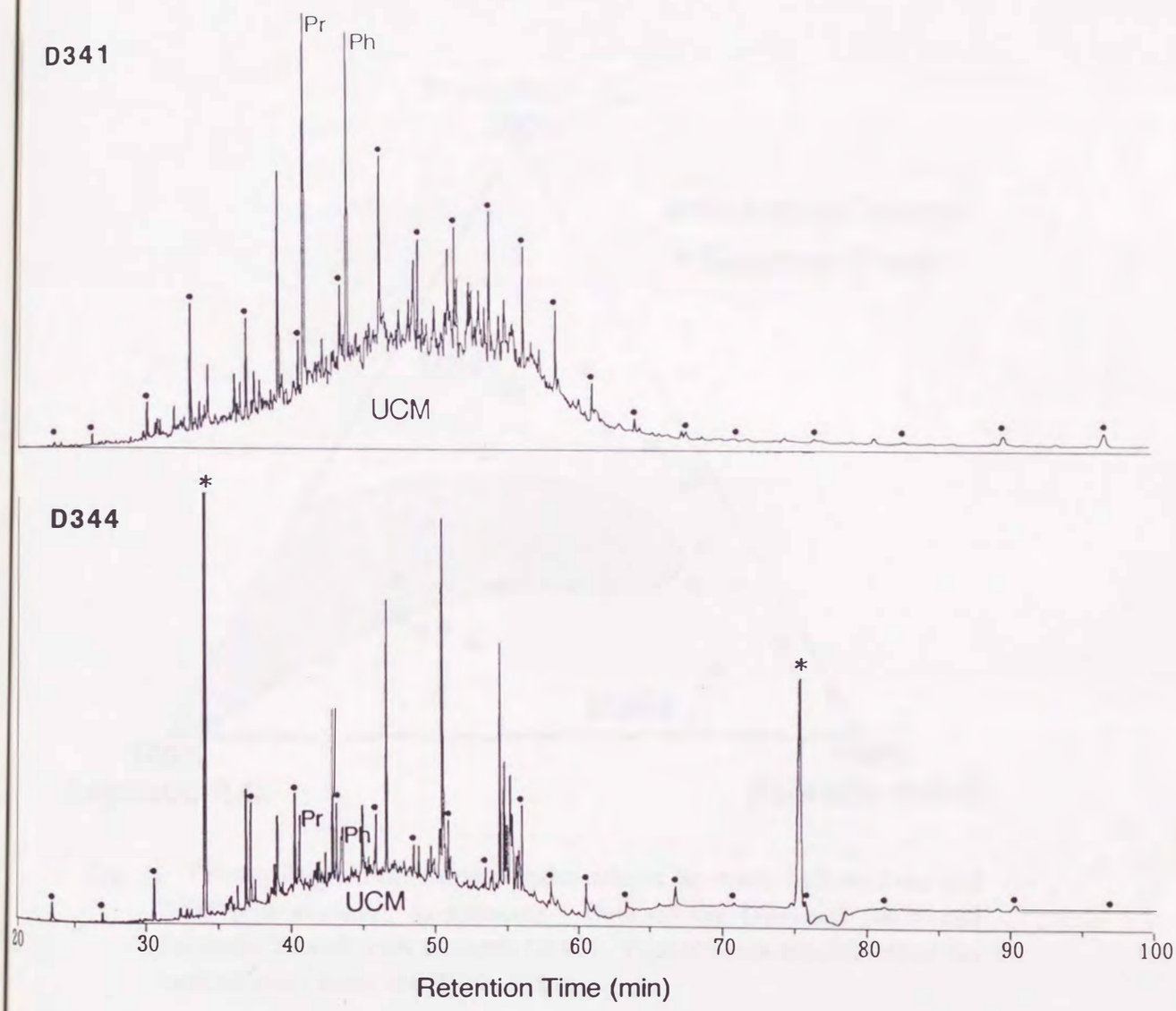

Fig. 29 TIC chromatograms of the aliphatic fractions in Samples D341 and D344 obtained from the northern part of Kagoshima Bay.

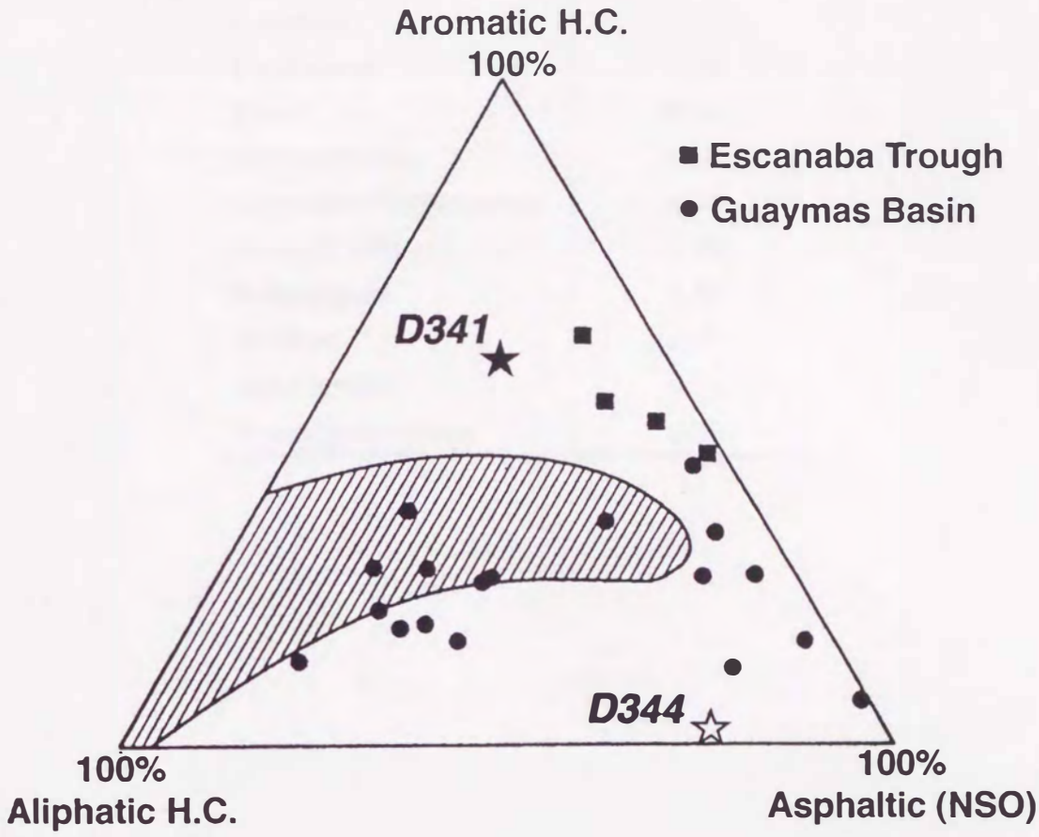

Fig. 30 Ternary diagram of saturated hydrocarbons, aromatic hydrocarbons and NSO plus asphaltic components. Data of the Guaymas Basin and Escanaba Trough from Simoneit (1993). Typical crude oils fall within the hatched area (Tissot and Welte, 1984).

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

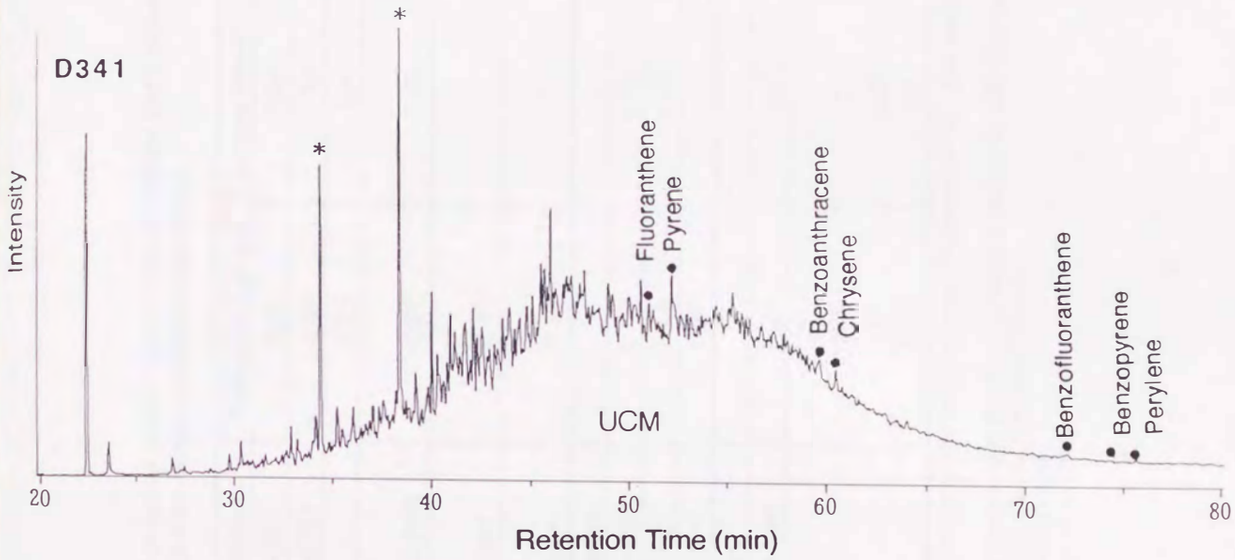

Fig. 31 TIC chromatogram of the aromatic fraction in Sample D341 from the Wakamiko Caldera. Rabeled peaks are major PAHs.

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

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 17β(H),21α(H)/17α(H),21β(H)	0.21	0.29	0.63
C31 Hopane (22R+22S)/C30αβ Hopane	0.62		
C32 Hopane (22R+22S)/C30αβ 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.
*** 5α-sterane (C21+C22)/(C21+C22+C27+C28+C29) ratio
†Ratios, as defind by Radke et al. (1982)
††Ratio, as defind by Garrigues et al. (1988)

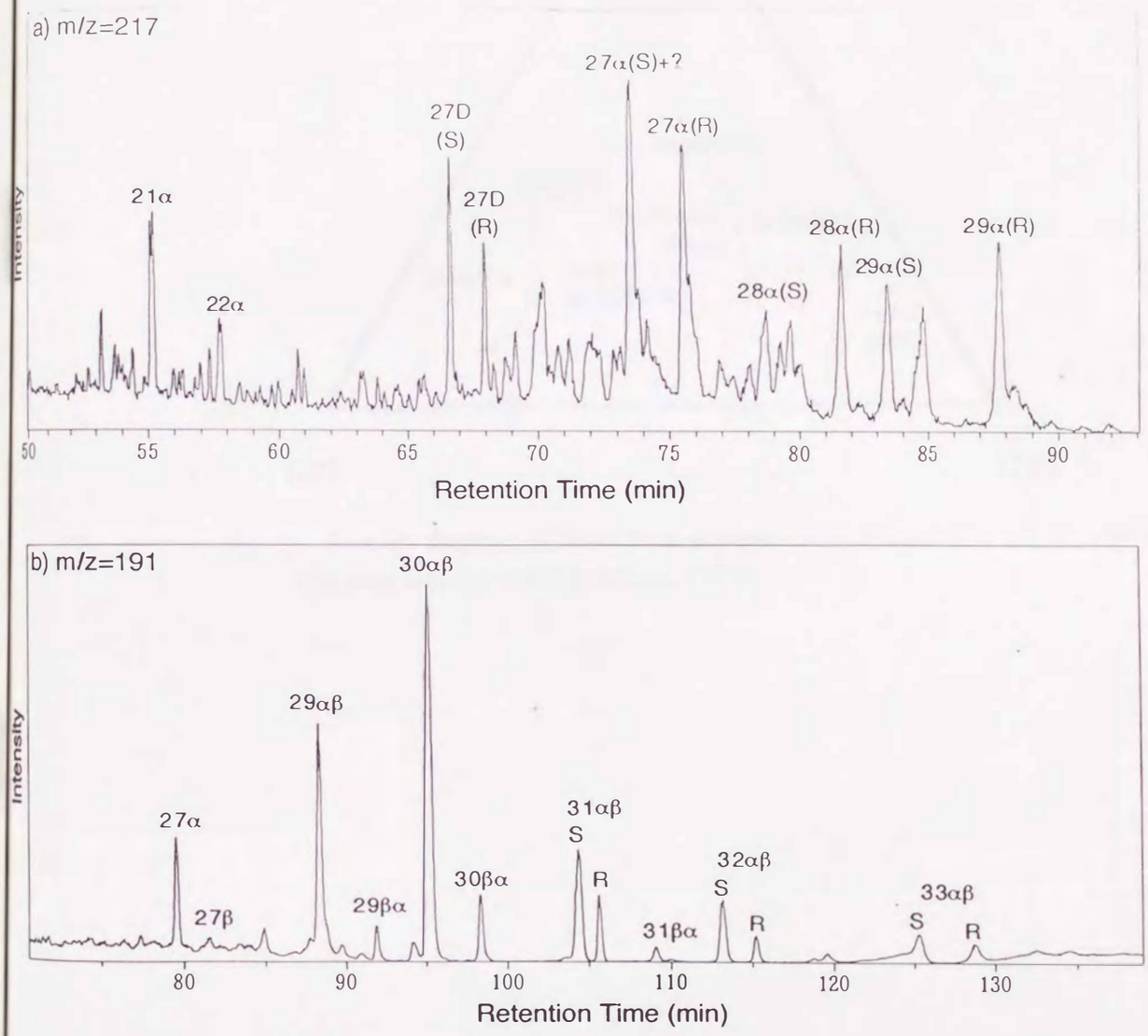

Fig. 32 Mass fragmentgram of biomarker steranes and triterpanes in Sample D341 from the Wakamiko Caldera.

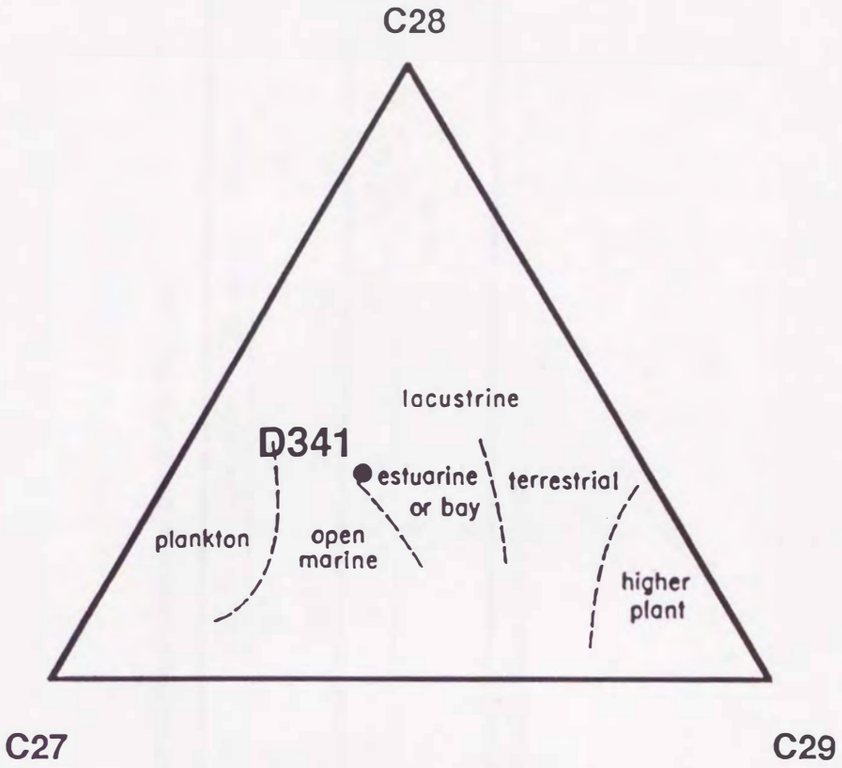

Fig. 33 Ternary diagram of Biomarker sterane compositions ($C_{27\sim29}$) as source indicator (Huang and Meinschein, 1979).

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_2H_6 ppm	C_3H_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	$\delta^{13}C_{PDB}$ methane ‰	δD_{SMOW} methane ‰	$\delta^{13}C_{PDB}$ CO_2 ‰	$\delta^{34}S_{CDT}$ H_2S ‰	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 C_{25}) and no carbon number preference, which are similar to that of conventional cruide oil. The CPI values of D916 and D921 sediments are 1.45 and 1.02, respectively. Small hump of the back ground, 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$0.16μg/g dry sediment), and higherly polycyclic aromatics could not identified. The pyrolitic 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 4.56μg/g dry sediment. CPI value of normal alkanes (C_{14}~C_{32}) in Sample D1030 was 2.1. Long chain alkanes were abundance in Sample D1030 and remarkable odd carbon number preference could been seen. CPI value of the alkanes longer than C_{24} was 4.1, indicating typical terrigenous input. Small hump of UCM of TIC chromatogram could been seen at the range of short chain alkanes (C_{16}~C_{26}). 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 pyrolitic origin PAHs such as pyrene and benzoanthracene were also detected.

5-2-3. Hydrocarbons in Myojin Caldera

Normal alkanes were identified ranging from C_{15} to C_{32} by GC/MS. Total concentrations of n-alkanes in D1008 and D1011 sediments were 4 and 4.8μg/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 ($>C_{26}$) 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 pyrolitic 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 μg/g	D921 μg/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

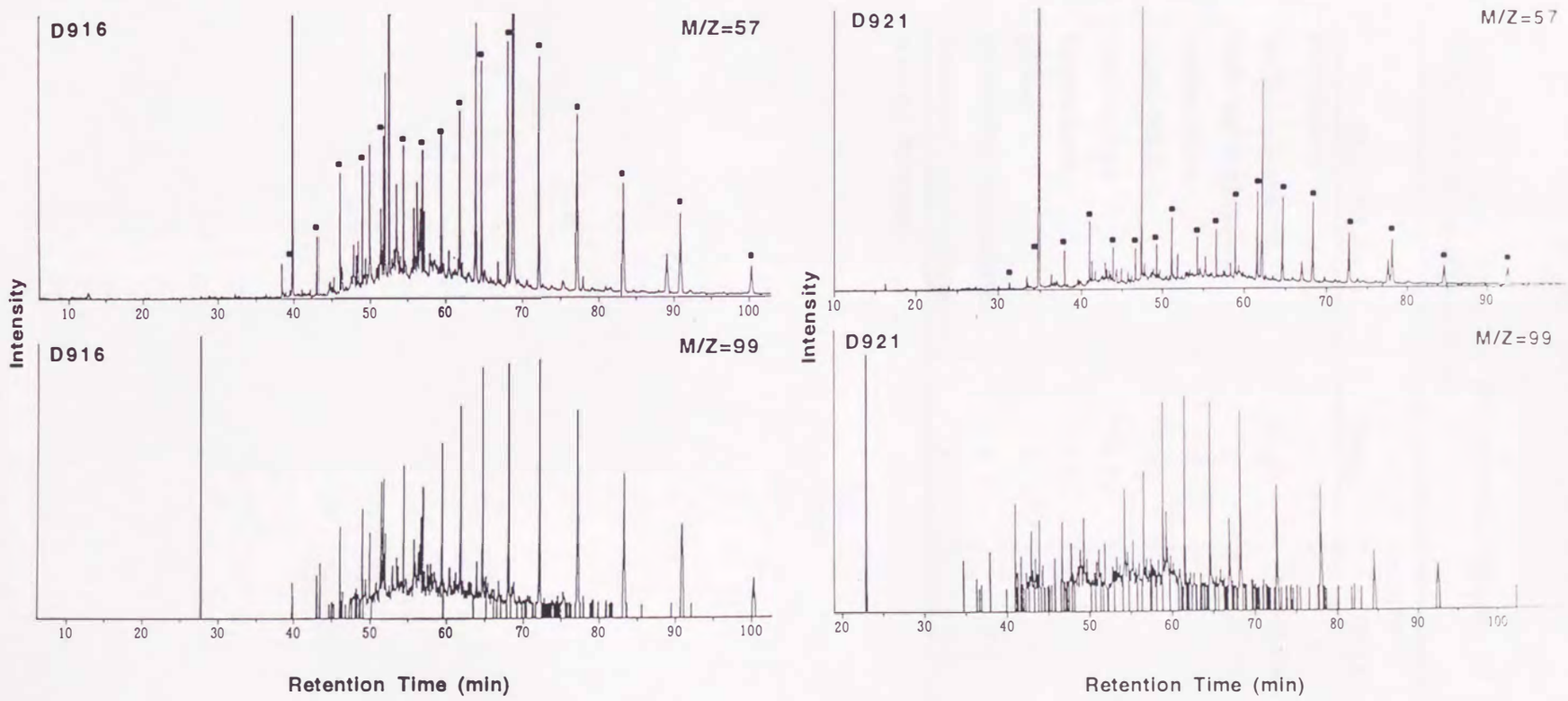

Fig. 34 Mass fragmentgrams (M/Z=57 and 99) of the aliphatic fractions in Samples D916 and D921 obtained from the DESMOS Caldera, Manus Basin.

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 sediemnt of the North Knoll, Iheya Ridge

Carbon number	D1030 μg/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
$CPI_{14\sim32}$	2.11
$CPI_{24\sim33}$	4.14
Pr/Ph	1.78

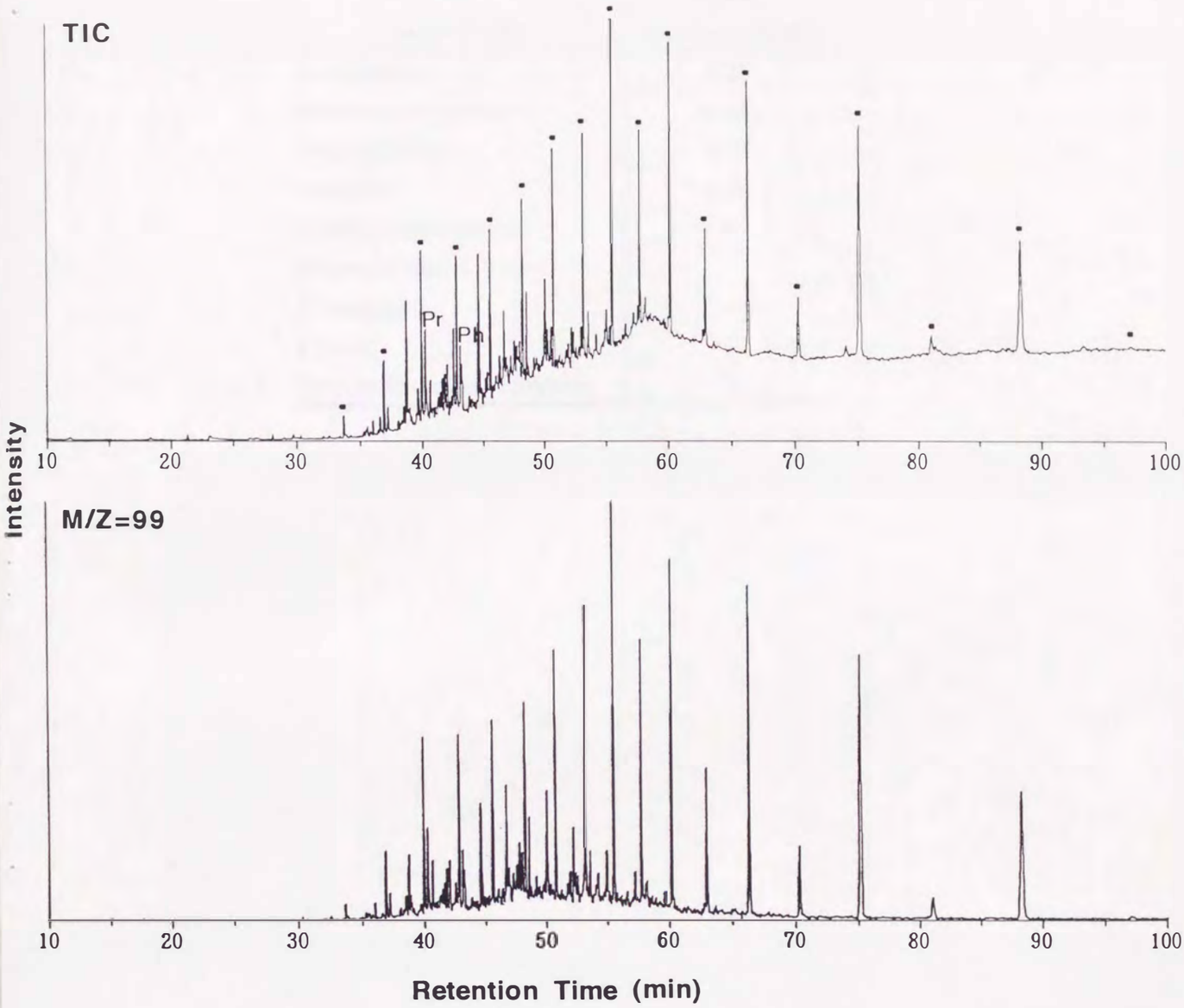

Fig. 35 TIC chromatogram of aliphatic fraction of Sample D1030 obtained from the North Knoll of Iheya Ridge, Okinawa Trough.

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 μg/g	D1011 μg/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

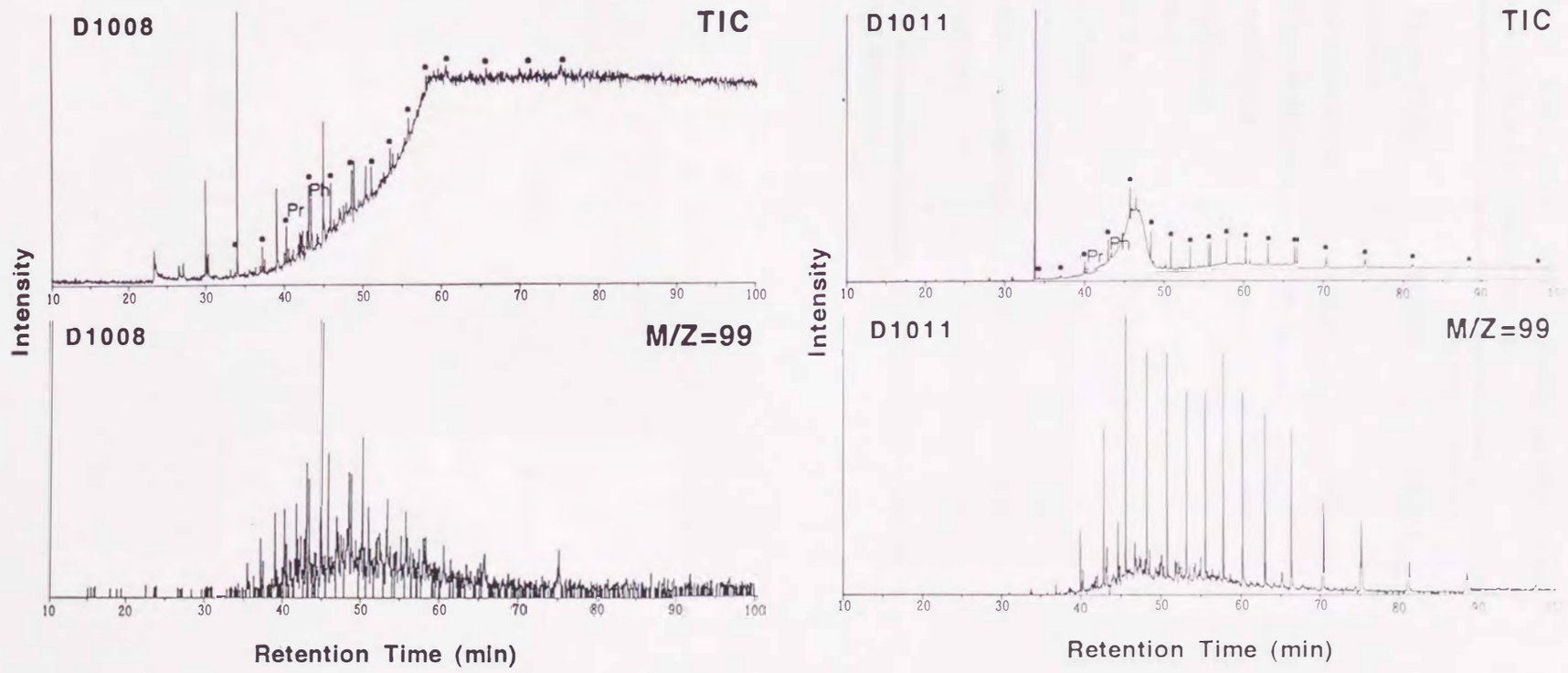

Fig. 36 TIC chromatograms and mass fragmentgrams of aliphatic fractions in Samples D1008 and D1011.

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 ($CPI_{24\sim33}=4.1$), 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 ($^3He/^4He=9.5X10^{-6}$) and carbon isotope ratios of CO_2 ($\delta^{13}C_{PDB}$ = -7.58 ~ -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), precence of pyrolitic PAHs is interpretated 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 detectedin these 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 C_{16} to C_{26}, suggesting precence 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 pail 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 resevoirs are also characterized by higher $\delta^{13}C$ 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 $\delta^{13}C$ 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 $\delta^{34}S$ 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 $\delta^{34}S$ 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 ($^3He/^4He$=6.90~8.67X10^{-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 ($^3He/^4He$=6.95X10^{-6}) is also as higher as that of 21°N East Pacific Rise ($^3He/^4He$=7.8X10^{-6}) (Lupton, 1983). The ratio of the fumarole in the caldera is also high ($^3He/^4He$=9.5X10^{-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-betl 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 $\delta^{34}S$ 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.

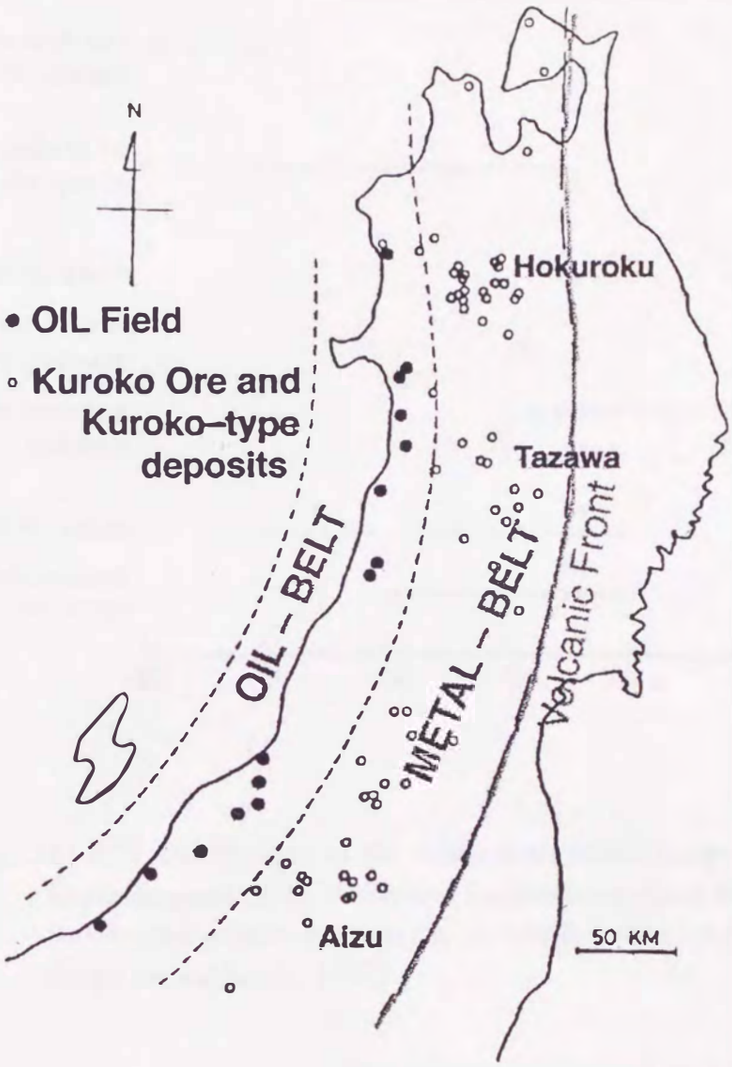

Fig. 37 Paired distribution of the metallic mineralization belt (Kuroko belt) and the oil-producing belt in the Neogene system of the northeast Japan (Kajiwara and Sasaki, 1987).

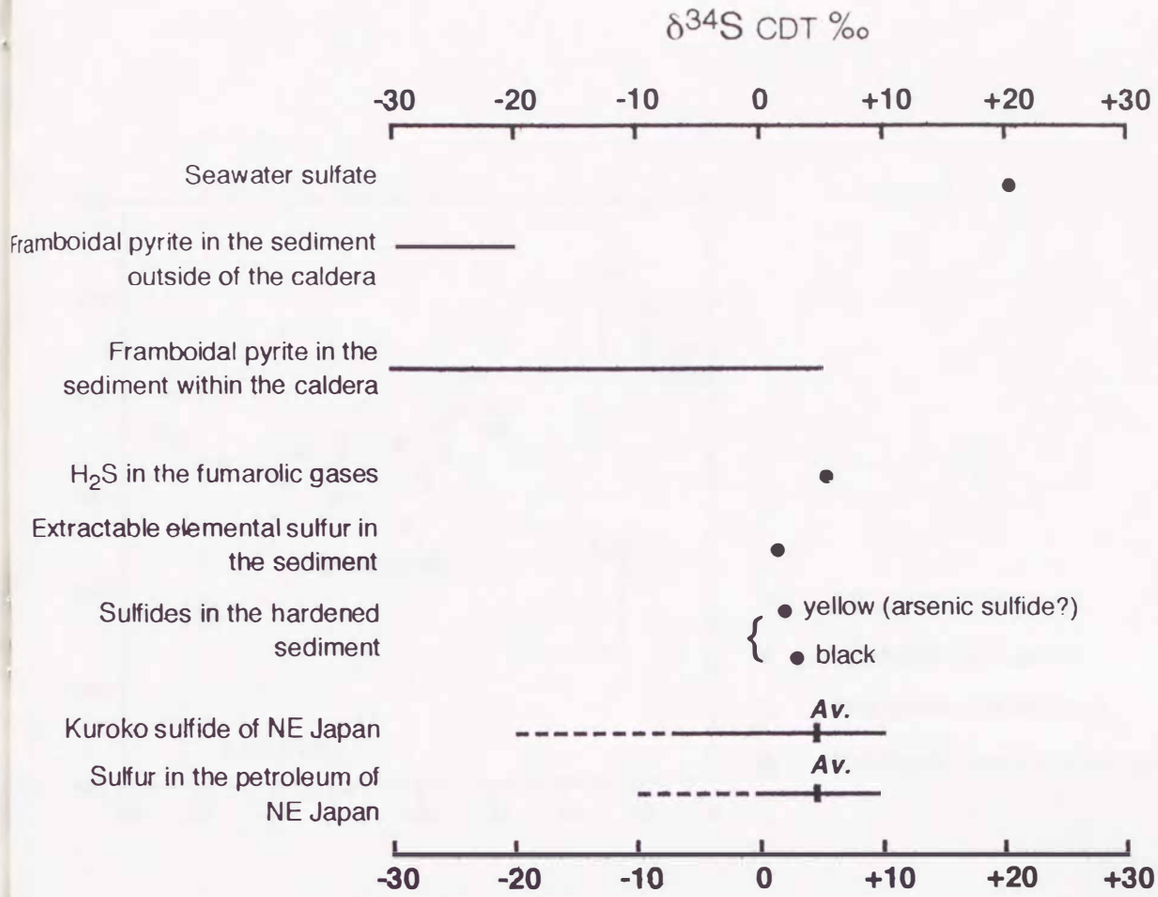

Fig. 38 $\delta^{34}S$ distributions of the sulfur compounds in the sediment and the fumarolic gases of the Wakamiko Caldera comparison with the Kuroko ore sulfides and organic sulfur in the petroleum yeilded in the northeast Japan (Kajiwara and Sasaki, 1987).

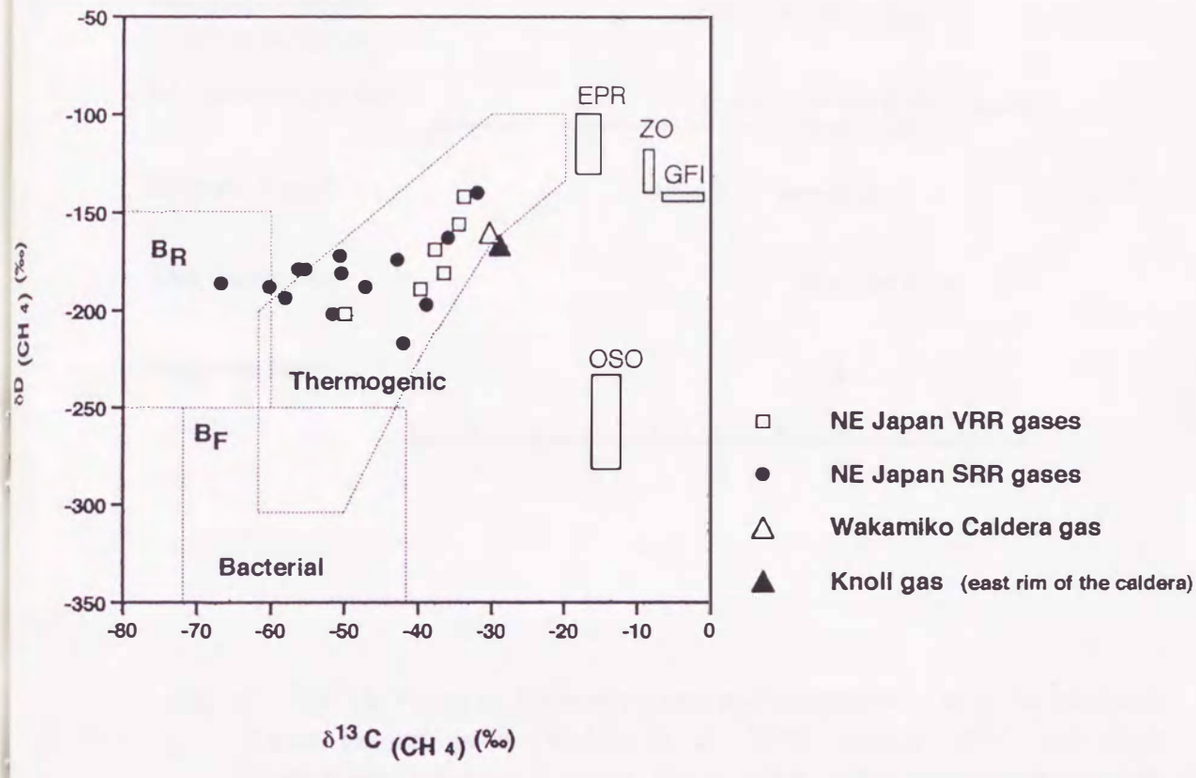

Fig. 39 Plot of δD *vs.* $\delta^{13}C$ of the methane in the fumarolic gases and natural gases of the northeast Japan (from Sakata, 1997). The boundary of bacteria and thermogenic methanes are drawn after Schoell (1988). The fields B_F and B_R are attributed to pathways of bacterial methanes from fermentation 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.

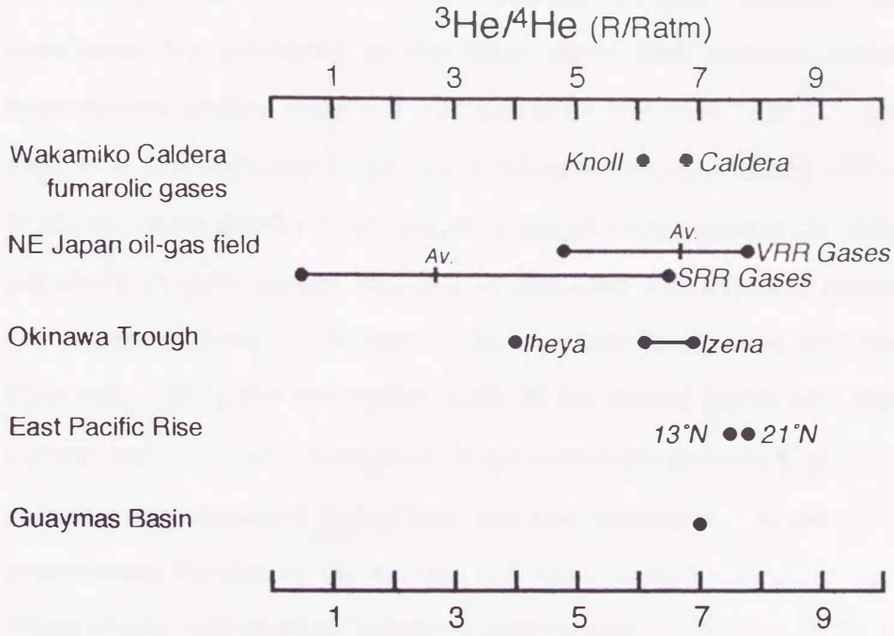

Fig. 40 $^3He/^4He$ ratios of fumarolic gases and comparisons with the northeast Japan naturel gases (Wakita et al., 1990; Sakata, 1997) and other hydrothermal systems (Lupton, 1983). SRR: sedimentary reservoir rock, VRR: volcanic reservoir rock.

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 voclano 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 petroleums (>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. Themost remarkable point is enrichment in monounsaturated fattyacids which are derived from aerobic bacterial metabolism. This is one of geochemical evidence for significant occurrence of bacterial chemosynthesis in hydrothermalareas0 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 significanthigh total fatty acid concentrations, the composition of thesebiomarker 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 terrigeneous 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.0: The fatty acids specifically derived from bacterial metabolism associated with hydrothermal activities is overwhelmed by significant supply of terrigeneous 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 terrigeneous 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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Reference

Alt, J. C., 1995, Subseafloor processes in mid-ocean ridge hydrothermal systems. In *Seafloor hydrothermal systems–Physical, chemical, biological and geological interactions*, S. Humphris, L. Mullineaux, R. Zierenberg and R. Thomson, **91**, Am. Geophys. Un., Washington, D.C., 85-114.

Aoki, M. and Nakamura, K., 1989, The occurrence of chimneys in Izena Hole No.2 ore body and texture and mineral composition of the sulfide chimneys. *JAMSTEC Deepsea Res.* **5**, 197-210.

Aramaki, S., 1984, Formation of the Aira Caldera, Southern Kyushu, ~22,000 years ago. *Jour. Geophys. Res.* **89**: 8485-8501.

Baird, B. H. and White, D. C., 1985, Biomass and community structure of the abyssal microbiota determined from the ester-linked phospholipids recovered from Venezuela Basin and Puerto Rico Trench sediments. Mar. Geol., **68**: 217-231.

Balkwill, D. L., Leach, F. R., Wilson, J. T., McNabb, J. F. and White, D. C., 1988, Equivalence of microbial biomass measures based on membrane lipid and cell wall components, adenosine triphoshate, and direct counts in subsurface auifer sediments. Microb. Ecol., **16**: 73-84.

Ballard, R. D., 1977, Notes on a major oceanographic find. Oceanus, **20**: 35-44.

Bernard, B. B., Brooks, J. M. and Sackett, W. M., 1976, Natural gas seepage in the Gulf of Mexico. Earth Planet. Sci. Lett., **31**: 48-54.

Binns, R. A. and Scott, S. D., 1993, Actively forming polymetallic sulfide deposits associated with felsic volcanic rocks in the eastern Manus back-arc basin, Papua New Gunea. Econ. Geol., **88**: 2226-2236.

Blake, J. A., Hecker, B., Grassle, J. F., Maciolek-Blake, N., Brown, B., Curran, M., Dade, B., Freitas, S. and Ruff, R. E., 1985, *Study of biological processes on the U. W. South Atlantic slope and rise. Phase 1. Benthic characterization study.* Final report. Prepared for U. S. Department of the Interior, Minerals Management Survice, Washinton D.C., under Contract No. 14-12-001-30064. 142 pp. + Appendices 1-4.

Blumer, M., 1957, Removal of elemental sulfur from hydrocarbon fractions, Analytical chemistry, **29**: 1039-1041.

Blumer, M., 1975, Curtisite, idrialite and pendletonite, polycyclic aromatic hydrocarbon minerals: Their composition and origin. Chem. Geol., **16**: 245-256.

Bobbie, R. J. and White, D. C., 1980, Characterization of benthic microbial community structure by high-resolution gas chromatography of fatty acid methyl esters. Appl. Environ. Microbiol., **39**: 1212-1222.

Boon, J. J., De Leeuw, J. W., van del Hoek, G. J. and Vosjan, J. H., 1977, Significance and taxonomic value of iso and anteiso monoenoic fatty acids and branched ß-hydroxy acids in *Desulfovibrio desulfuricans*. J. Bacteriol., **129**: 1183-1191.

Boon, J. J., W. Liefkens, Rijpstra, W. I. C., Baas, M. and De Leeuw, J. W., 1978, Fatty acids

of *Desulfovibrio desulfuricans* as marker molecules in sedimentry environments. In *Environmental and geomicrobiology biogeochemistry*, ed., Krumbein, W. E., Ann Arbor Science Publisher, Ann Arbor, Mich, p. 355-372.

Canuel, E. and Martens, C. S., 1992, Seasonal variations in the sources and alteration of organic matter association with recently-deposited sediments. Org. Geochem., **20**: 563-578.

Chiba, H., Nakashima, K., Gamo, T., Ishibashi, J., Tsunogai, U. and Sakai, H., 1993, Hydrothermal activity at the Minami-Ensei Knoll, Okinawa Trough: Chemical characteristics of hydrothermal solutions. Proc. JAMSTEC Symp. Deep Sea Res., **9**: 271-282.

Chiba, H., Ishibashi, J., Ueno, H., Oomori, T., Uchiyama, N., Takeda, T., Takamine, C., Ri, J. and Itomitsu, A., 1996, Seafloor hydrothermal systems at North Knoll, Iheya Ridge, Okinawa Trough. JAMSTEC J. Deep Sea Res., **12**: 211.

Cooper, J.E. and Bray, E.E., 1963, A postulated role of fatty acids in petroleum formation. Geochim. Cosmochim. Acta, **27**: 1113-1127.

Corliss, J. B., Dymond, J., Gordon, L. I., Edmond, J. M., Von Herzen, R. P., Ballard, R. D., Green, K., Williams, D., Bainbridge, A., Crane, K. and Van Andel, T. H., 1979, Submarine thermal springs on the Garapagos Rift. Science, **203**: 1073-1083.

Initial reports of the Deep Sea Drilling Project, Curray, J. R., Moore, D. G., Aguayo, J. E., Aubry, M. P., Einsele, G., Fornari, D. J., Gieskes, J., Guerrero, J. C., Kastner, M., Kelts, K., Lyle, M., Matoba, Y., Molina-Cruz, A., Niemitz, J., Rueda, J., Saunders, A. D., Schrader, H., Simoneit, B. R. T. and Vacquier, V., Ed., U.S. Goverment Printing Office: Washington, D.C., 1982, Vol. **64**.

Davis, E. E., Mottle, M., Fisher, A., Baker, P. A., Becker, K., Boni, M., Boulègue, J. J., Brunner, C. A., Duckworth, R. C., Franklin, J. M., Goodfellow, W. D., Gröschel-Becker, H. M., Kinoshita, M., Konyukhov, B. A., Körner, U., Krasnov, S. G., Langseth, M., Mao, S.,Marchig, V., Marumo, K., Oda, H., Rigsby, C. A., Simoneit, B. R. T., Stakes, D. S., Villinger, H. W., Wheat, C. G., Whelan, J. and Zierenberg, R. A., 1992, Hot rocks and massive sulfide: northern Juan de Fuca Ridge, EOS, **73**: 193, 196-198.

De Rose, M., Gambacorta, A. and Gliozzi, A., 1986, Structure, biosynthesis, and physicochemical properties of archaebacterial lipids. Microbiol. Rev., **50**: 70-80.

Didyk, B. M. and Simoneit, B. R. T., 1990, Petroleum characteristics of the oil in a Guaymas Basin hydrothermal chimney. In *Organic matter alteration in hydrothermal systems – Petroleum generation, migration and biogeochemistry*. ed. Simoneit, B. R. T., Appl. Geochem., **5**: 29-40.

Durand, P., Reysenbach, A. L., Prieur, D. and Pace, N., 1993, Isolation and characterization of Thiobacillus hydrothermalis sp. Nov., a mesophilic obligately chemolithotrophic bacterium isolated from a deep-sea hydrothermal vent in Fiji Basin. Arch. Microbiol.,

159: 39-44.

Einsele, G., 1985, Basaltic sill–sediment complexes in young spreading centers: genesis and significance. Geology, **13**: 249-252.

Edlund, A., Nichols, P. D., Roffey, R. and White, D. C., 1985, Extractable and lipopolysaccharide fatty acid and hydroxy acid profiles from *Desulfovibrio* species. J. Lipid Res., **26**: 982-988.

Findlay, R. H. and Dobbs, F. C., 1993, Quantitative description of microbial communities using lipid analysis. In *Handbook of methods in aquatic microbial ecology*, eds., Kamp, P. F., Sherr, B. F., Sherr, E. B. and Cole, J. J., Lewis, Florida, 271-284.

Findlay, R.H., Fell, J. W., Coleman, N. K. and Vestal, J. R., 1986, Biochemical indicators of the role of fungi and thraustochy trids in mangrove detrital systems. In *Biology of marine fungi*, ed., Moss, S. T., Cambridge University Press, Cambridge, p. 91-104.

Fujioka, K., 1983, Where were the "Kuroko deposits" formed, looking for the present day analogy. Min. Geol. Spec. Issue, **11**: 55-68.

Fujioka, K., 1997, Science of deep seafloor, NHK Books, NHK Publishing Association, Tokyo, p.249..

Fujioka, K., Kinoshita, M., Soh, W., Tsukawaki, J., Ashi, J., Akimoto, K. and Watanabe, M., 1989, Geology of Sagami Bay and its environs –reports on the results of KT88-1 cruise –. Bull. Earthq. Res. Inst., **64**: 391-431.

Fukushima, K. and Ishiwatari, R., 1984. Acid and alcohol compositions of wax esters in sediments from different environments. Chem. Geol., **47**: 41-56.

Gamo, T., Ishibashi, J., Shitashima, K., Kinoshita, M., Watanabe, M., Nakayama, E., Sohrin, Y., Kim, E.-S., Masuzawa, T. and Fujioka, K., 1988, Anomalies of bottom CH_4 and trace metal concentrations associated with high heat flow at the Calyptogena community off Hatsushima Island, Sagami Bay, Japan: A preliminary report of Tansei Maru KT-88-1 cruise Leg-1. Geochem. J., **22**: 215-230.

Gamo, T., Okamura, K., Charlou, J. L., Urabe, T., Auzende, J. M., Shipboard Scientific Party of the ManusFlux Cruise, Ishibashi, J., Shitashima, K. and Kodama, Y., 1996, Chemical exploration of hydrothermal activity in the Manus Basin, Papua New Guinea. JAMSTEC J. Deep Sea Res., **12**: 335-345.

Gamo, T., Okamura, K., Charlou, J. L., Urabe, T., Auzende, J. M., Ishibashi, J., Shitashima, K., Chiba, H. and Shipboard Scientific Party of the ManusFlux Cruise, 1997, Acid and sulfate rich hydrothermal fluids from the Manus back-arc basin, Papua New Guinea. Geology, **25**: 139-142.

Gamo, T., Sakai, H., Ishibashi, J., Oomori, T., Chiba, H., Shitashima, K., Nakashima, K., Tanaka, Y. and Masuda, H., 1991a, Growth mechanism of the hydrothermal mounds at the CLAM Site, Mid Okinawa Trough, inferred from their morphological, mineralogical, and chemical characteristics. JAMSTECTR Deepsea Res., 7: 163-184.

Gamo, T., Sakai, H., Kim, E.-S., Shitashima, K. and Ishibashi, J., 1991b, High alkalinity due

to sulfate reduction in the CLAM hydrothermal field, Okinawa Trough. Earth Planet. Sci. Lett., **107**: 328-338.

Geissman, T. A., Sim, K. Y. and Murdoch, J., 1967, Organic minerals. Picene and chrysene as constituents of the mineral curtisite (idrialite). Experientia, **23**: 793-794.

Gena, K., Mizuta, T., Ishiyama, D. and Urabe, T., 1997, Geochemical characteristics of altered basaltic andesite by sulfuric-acidic rich solution from the Desmos Caldera, Manus Basin, Papua New Guinea. JAMSTEC J. Deep Sea Res., **13**: 269-285.

Gill, J. B. and Gorton, M., 1973, A proposed geological and geochemical history of eastern Melanesia, In *The western Pacific: Island arcs, marginal seas and geochemistry*, ed. Coleman, P. J., University of Western Australia Press, 543-566.

Gillan, F. T. and Hogg, R. W., 1984, A method for the estimation of bacterial biomass and community structure in mangrove associated sediments. J. Microbiol. Methods, **2**: 275-293.

Gillan, F. T., Johns, R. B., Verhey, T. V., Nichols, P. D., Esdail, R. J. and Bavor, H. J.,1983, Monounsaturated fatty acids as specific bacterial biomarkers in marine sediment. In Advances in organic geochemistry 1981, ed., Bjoroy, M., John Wiley & Sons, Inc., New York, p. 198-206.

Grassle, J. F., 1985, Hydrothermal vent animals: distribution and biology. Science, **229**: 713-717.

Guckert, J. B., Ringelberg, D. B. and White, D. C., 1987, Biosynthesis of *trans* fatty acids from acetate in the bacterium Pseudomonas atlantica. Can. J. Microbiol., **3**: 748-754.

Halbach, P., Nakamura, K., Wahsner, M., Lange, J., Sakai, H., Kaselitz, L., Hansen, R.-D., Yamano, M., Post, J., Prause, B., Seifert, R., Michaelis, W., Teichmann, F., Kinoshita, M., Marten, A., Ishibashi, J., Czerwinski, S. and Blum, M., 1989, Probable modern anologue of Kuroko-type massive sulphide deposits in the Okinawa Trough back-arc basin. Nature, **338**: 496-944.

Hannington, M. D., Jonasson, I. R., Herzig, P. M. and Petersen, S., 1995, Physical and chemical processes of seafloor mineralization at Mid-Ocean Ridges. In *Seafloor hydrothermal systems–Physical, chemical, biological and geological interactions*, S. Humphris, L. Mullineaux, R. Zierenberg and R. Thomson, **91**, Am. Geophys. Un., Washington, D.C., 115-157.

Harvey, H. R., 1994, Fatty acids and sterols as source markers of organic matter in sediments of the North Carolina continental slope. Deep-Sea Res. II, **41**: 783-796.

Harvey, H.R., Eglington, G., O'Hara, S.C.M. and Corner, E.D.S., 1987, Biotransformation and assimilation of dietary lipids by Calanus feeding on a dinoflagellate. Geochim. Cosmochim. Acta, **51**: 3031-3040.

Hashimoto, J. and Hotta, H., 1994, Observation of chemosynthetic communities by means of the submersible *Shinkai 2000* in Sagami Bay. Bull. Japan Soc. Fish. Oceanorg., **58**: 194-198.

Hashimoto, J., Matsuzawa, S. and Hotta, H., 1988, Searching for biological communities at the Okinoyama Bank site. Tech. Rep. Jpn. Mar. Sci. Tech. Cent. (JAMSTEC). Spec. Iss., **4**: 177-188.

Hashimoto, J., Ohta, S., Tanaka, T., Hotta, H., Matsuzawa, S. and Sakai, H., 1989, Deep-sea communities dominated by the giant clam Calyptogena soyoae, along the slope foot of Hatsushima Island, Sagami Bay, Central Japan. Palaeogeogr. Palaeoclimatol. Palaeoecol., **71**: 179-192.

Hashimoto, J., Fujikura, K. and Hotta, H., 1990, Observations of deep sea biological communitiesat the Minami-Ensei Knoll. JAMSTECTR Deep-sea Res., **6**: 167-179.

Hashimoto, J., Fujikura, K., Ohta, S. and Miura, T., 1993a, Observations of deep sea biological communitiesat the Minami-Ensei Knoll–II. Proc. JAMSTEC Symp. Deep Sea Res. **9**: 327-336.

Hashimoto, J., Miura, T., Fujikura, K. and Ossaka J., 1993b, Discovery of vestimentiferan tube-worms in the euphotic zone. *Zool. Sci.* **10**: 1063-1067.

Hashimoto, J. and Ohta, S., 1997, Hydrothermal vent field and vent-associated biological communities in the Manus Basin. In *Cruise report of the BIOACCESS Cruise '96 in the Manus Basin*, JAMSTEC, p.241.

Hattori, M., Kanie, Y., Oba, T., Akimoto, K. and Kanno, S., 1996, Environmental conditions of carbonates and Chemosynthetic animal communities associated with cold seepage zones along the subduction zone in Sagami Bay and other land areas in Japan. JAMSTEC J. Deep Sea Res., **12**: 117-131.

Hayasaka, S., 1987, Geologic structure of Kagoshima Bay, South Kyushu, Japan. *Mono. Assoc. Geol. Collab.* **33**: 225-233.

Hedrick, D. B., Pledger, R. D., White, R. D. and Baross, J. A., 1992, In situ microbial ecology of hydrothermal vent sediments. FEMS Microbiol. Ecol., **101**: 1-10.

Hessler, R. R. and Kaharl, V. A., 1995, The deep-sea hydrothermal vent community: an overview. In *Seafloor hydrothermal systems–Physical, chemical, biological and geological interactions*, S. Humphris, L. Mullineaux, R. Zierenberg and R. Thomson, **91**, Am. Geophys. Un., Washington, D.C., 72-84.

Horikoshi, E., 1977, Tectonics of ore formation. In *Gendai koshogaku no kiso*, ed. Tatsumi, T., Univ. Tokyo Press, Tokyo, p. 32-43.

Horikoshi, E., 1981, Volcanism and tectonics of the NE Japan Arc in time and space. Abstract of IAVCEI symposium, Japan, pp. 137-138.

Huang, W. and Meinschein, W. G., 1979, Sterols as ecological indicators. Geochim. Cosmochim. Acta, **43**: 739-745.

Hunt, J. M., 1979, *Petroleum geochemistry and geology*. W.H. Freeman and Company, San Francisco, 617p.

Iizasa, K., Ishibashi, J., Fujiwara, Y., Hashimoto, J., Horii, Y., Ishizuka, O., Koyama, S. and Yuasa, M., 1998, Active hydrothermal field associated with black smoker in the Myojin

Knoll, Izu-Ogasawara arc, northwestern Pacific., JAMSTEC J. Deep Sea Res., **14** (in press).

Iizasa, K., Naka, J., Yuasa, M. and Fiske, R. S., 1997, Sulfide chimnys and massive sulfides at Myoujin knoll caldera, Izu-Ogasawara arc. JAMSTEC J. Deep Sea Res., **13**: 443-456.

Ishibashi, J. Sano, Y., Wakita, H., Gamo, T., Tsutsumi, M. and Sakai, H., 1990, Geochemical studies on the hydrothermal activty in the Mid-Okinawa Trough: Characterization of hydrothermal fluids from chemical and isotopical composition of the gas components. JAMSTECTR Deepsea Res., **6**: 63-68.

Ishibashi, J. and Urabe, T., 1995, Hydrothermal activity related to arc-backarc magmatism in the western Pacific. In Backarc Basin, ed. Taylor, B., Plenum Press, New York, p. 451-495.

Ishibashi, J., Yamanaka, T., Tsunogai, U., Yoshida, M., Shitashima, K., Okamura, K., Gamo, T. and Onboard Scientists of RV Natsushima, 1998, Geochemical features of hydrothermal activity in Myojin Knoll, Izu-Ogasawara Arc, Abst. Shinkai Symp., JAMSTEC, Tokyo, p. 139.

Ishiwatari, R., 1988. Inflow and deposition of terrigenous organic matter into the Tokyo Bay. Engankaiyou kenkyuu note, **25**: 127-133.

Ishiwatari R. and Fukushima, K., 1979, Generation of unsaturated and aromatic hydrocarbons by thermal alteration of young kerogen. Geochim. Cosmochim. Acta, **43**: 1343-1349.

Jannasch, H. W. and Wirsen, C. O., 1979, Chemosynthetic primary production at East Pacific sea floor spreading center. Bioscience, **29**: 592-598.

Jannasch, H. W., 1983, Microbial processesat deep-sea hydrothermal vents. In *Hydrothermal processes at sea floor spreading centers*, P. A. Rona, K. Boström, L. Laubier and K. L. Smith, Plenum Press, New York, 677-709.

Jannasch, H. W., 1989, Litho-autotrophically sustained ecosystems in the deep sea. In *Biology of autotrophic bacteria*, H. G. Schlegel and B. Bowien, Sci. Tech. Publ., Madison, WI., 147-166.

Jannasch, H. W., 1995, Microbial interactions with hydrothermal fluids. In *Seafloor hydrothermal systems–Physical, chemical, biological and geological interactions*, S. Humphris, L. Mullineaux, R. Zierenberg and R. Thomson, **91**: Am. Geophys. Un., Washington, D.C., 273-296.

Japanese DELP Research Group on Back-Arc Basins, 1991, Report on DELP 1988 cruises in the Okinawa Trough: Part 1. General outline. Bull. Eartquake Res. Inst. Univ. Tokyo, **66**: 1-16.

Kadko, D., Baross, J. and Alt, J., 1995, The magnitude and global implications of hydrothermal flux. In *Seafloor hydrothermal systemss–Physical, chemical, biological and geological interactions*, S. Humphris, L. Mullineaux, R. Zierenberg and R. Thomson, **91**, Am. Geophys. Un., Washington, D.C., pp. 446-466.

Kajiwara, Y. and Sasaki, A., 1987, Sulfur isotope similarity between crude oils and Kuroko

sulfides from the Green Tuff region of northeastern Japan. *Mining Geol.* **37**, 199-203.

Kamata, M., Yonehara, N., Sakamoto, H. and Ohnishi, T., 1978, Distribution of the trace elements and the circulation process of sea water in the inner bay sea water.– an example at the Kagoshima Bay–. *Collected reports of special project research "Preservation of marine environment"* (Takahashi, A. ed.), 49-54.

Kaneda, T., 1977, Fatty acids of the genus Bacillus: an example of branched chain preference. Bacteriol. Rev., 41: 391-418.

Kanie, Y., Hattori, M. and Sasahara, Y., 1992, Two types of clam communities in Sagami Bay, Central Japan: Geologic settings and the tertiary records in the Miura and Boso Peninsulas. Sci. Rep. Yokosuka City Mus., **40**: 37-43.

Kanie, Y., Hattori, M., Okada, H. and Akimoto, K., 1996, Microfossil age of the Okinoyama Bank Chain in Sagami Bay, south-central Japan and developmental history of the subduction zone of Sagami Trough. JAMSTEC Deep Sea Res., **12**: 101-106.

Katayama-Fujimura, Y., Tsuzaki, N. and Kuraishi, H., 1982, Ubiquinone, fatty acid and DNA base composition determination as a guide to the taxonomy of the genus *Thiobacillus*. J. Gen. Microbiol., **128**: 1599-1611.

Kawka, O. E. and Simoneit, B. R. T., 1990, Polycyclic aromatic hydrocarbons in hydrothermal petroleums from the Guaymas Basin spreading center. *Appl. Geochem.* **5**: 17-27.

Kawka, O. E. and Simoneit, B. R. T., 1994, Hydrothermal pyrolysis of organic matter in Guaymas Basin: I. Comparison of hydrocarbon distributions in subsurface sediments and seabed petroleums. Org. Geochem., **22**: 947-978.

Kerger, B. D., Nichols, P. D., Antworth, C. P., Sand, W., Bock, E., Cox, J. C., Langworthy, T. A. and White, D. C., 1986, Signature fatty acids in the polar lipids of acid-producing Thiobacillus spp.: Methoxy, cyclopropyl, alpha-hydroxy-cyclopropyl and branched and normal monoenoic fatty acids. FEMS Microbiol. Ecol., **38**: 677.

Killops, S. D. and Killops V. J., 1993, *An introduction to Organic Geochemistry*. Lomgman, London, p.265.

Kimura, M., 1985, Back-arc rifting in the Okinawa Trough. Mar. Petrol. Geol., **2**: 222-240.

Kimura, M., Kaneko, I., Kato, Y., Yamamoto, S., Kushiro, I., Tokuyama, H., Kinoshita, H., Isezaki, N., Masaki, H., Ohshida, A., Uyeda, S.and Hilde, T. W. C., 1986, Report on DELP 1984 cruise in the Okinawa Trough 5: topography and geology of the central grabens and their vicinity. Bull. Earthq. Res. Inst. Univ. Tokyo, **61**: 269-310.

Kitazato, H., 1979, Marine paleobathymetry and paleotopography of the Hokuroku district during the time of the Kuroko deposition, based on foraminiferal assemblages. *Mining Geol.* **29**: 207-216.

Kobayashi, K. and Nakamura, K., 1986, Tectonics of spreading of marginal sea. In *Formation of Japan Islands*, Eds. Taira, A. and Nakamura, K., Iwanami, Tokyo, pp. 158-165.

Kulm, L. D., Suess, E., Moore, J. C., Carson, B., Lewis, B. T., Ritger, S. D., Kadko, D. C.,

Thornburg, T. M., Embley, R. W., Rugh, W. D., Massoth, G. J., Langseth, M. G., Cochrane, G. R. and Scamman, R. L., 1986, Oregon subduction zone; venting, fauna, and carbonates. Science, **231**: 561-566.

Kvenvolden, K. A. and Simoneit, B. R. T., 1990, Hydrothermally derived petroleum: Examples from Guaymas Basin, Gulf of California, and Escanaba Trough, Northeast Pacific Ocean. *AAPG Bulletin* **74**: 223-237.

Laubier, L. and Desbruyères, D., 1985, Oases at the bottom of the ocean. Endeavour, New Series, **9**: 67-76.

Lechevalier, M. P., 1977, Lipid in bacterial taxonomy – a taxonomist's view. Crit. Rev. Microbiol., **5**: 109-210.

Lonsdale, P., 1977, Clustering of suspension feeding macrobenthos near abyssal hydrothermal vents at oceanic spreading centers. Deep-Sea Res., **24**: 857-863.

Lonsdale, P., 1985, A transform continental margin rich in hydrocarbons, Gulf of California. AAPG Bull., **69**: 1160-1180.

Lonsdale, P. and Becker, K., 1985, Hydrothermal plumes, hot springs, and conductive heat flow in the Southern Trough of Guaymas Basin. Earth Planet. Sci. Lett., **73**: 211-225.

Lowell, R. P. and Rona, P. A., 1985, hydrothermal models for the generation of massive sulfide ore deposits. J. Geophys. Res., **90**: 8769-8783.

Lupton, J. E., 1983, Fluxes of ^{3}He and heat from submarine hydrothermal systems: Guaymas Basin versus 21°N EPR. *EOS (Transactions, AGU)* **64**: 723.

Mancuso, C. A., Franzmann, P. D., Burton, H. R. and Nichols, P. D., 1990, Microbial community structure and biomass estimates of a methanogenic Antarctic Lake ecosystem as determined by phospholipid analyses. Microb. Ecol., **19**: 73-95.

Masuzawa, T., Nakatsuka, T. and Nobuyuki, H., 1995, Geochemistry of pore waters from a bathyal Calyptogena community off Hatsushiama Island, Sagami Bay, Japan. In Biogeochemical processes and ocean flux in the Western Pacific, eds., Sakai, H. and Nozaki, Y., TERRAPUB, Tokyo, pp. 407-421.

Masuzawa, T., Handa, N., Kitagawa, H. and Kusakabe, M., 1992, Sulfate reduction using methane in sediments beneath a bathyal "cold seep" giant clam community off Hatsushima Island, Sagami Bay, Japan. Earth Planet. Sci. Lett., **110**: 39-50.

Masuzawa, T. and Kitano Y., 1983, Interstitial water chemistry in deep-sea sediments from the Japan Sea. Journal of the Oceanogaphical Society of Japan, **39**: 171-184.

Mita, N. and Maeda, M., 1988, Marine bacterial biomass: its estimetion and application to prospecting of submarine hydrothermal activity. Chikyukagaku (geochemistry), **22**: 106-113.

Mosier, D. L., Singer, D. A. and Salem, B. B., 1983, Geologic and grade-tonnage information on volcanic -hosted copper-zinc-lead massive sulfide deposits. U. S. G. S. Open-file rep. 83-89.

Naganuma, T., Fujikura, K., Naka, J., Kato, Y. and Takeuchi, A., 1996, Sedimentary fatty

acids from fissured seafloor in the northern Okushiri Ridge: comparison with those from a methane seep and a submarine volcano. JAMSTEC J. Deep Sea Res., **12**: 83-94.

Naka, J., Fujikura, K. and Hashimoto, J., 1991, New geological information of Calyptogena colony off Hatsushima Island, Sagami Bay. JAMSTECTR Deep Sea Res., **7**: 1-6.

Nakano, T., Kajiwara, Y. and Farrell, C.L., 1989, Strontium isotope constraint on the genesis of crude oils, oil-field brines, and Kuroko ore deposits from the Green Tuff region of northeastern Japan. *Geochim. Cosmochim. Acta* **53**: 2683-2688.

Nedachi, M., Miura, T. and Hashimoto, J., 1997, The behavior of sulfur compounds asociated with fumaloric activities in Kagoshima Bay. *Proceeding of 14th Shinkai symposium*, 35-36.

Nedachi, M., Ueno, H., Oki, K., Shiga, Y., Hayasaka, S. Ossaka, J., Nogami, K., Ito, N. and Hashimoto, J., 1991, Sulfide veinlets and the surrounding marine sediments in the fumarole area in the Wakamiko Caldera, northern Kagoshima Bay. *JAMSTEC Deepsea Res.* 7, 235-243.

Ohkouchi, N., 1990, Active geological structures and tectonics in Sagami Bay Area. Chigaku Zasshi, **99**: 458-470.

Ohmoto, H., 1978, Submarine caldera: a key to the formation of volcanic massive sulfide deposits. Minning Geol., **28**: 219-231.

Ohmoto, H., 1996, Formation of volcanogenic massive sulfide deposits: the kuroko prespective. Ore Geol. Rev., **10**: 135-177.

Ohta, S., 1983, Photographic census of large-sized benthic organisms in the bathyal zone of Suruga Bay, central Japan. Bull. Ocean Res. Inst. Univ. Tokyo, **15**: 1-244.

Ohta, S., 1988, Biological processes at hydrothermal vents. Chikyukagaku, **22**: 87-95.

Ohta, S., 1990, Deep-sea submarsible survey of the Hydrothermal vent community on the northeastern slope of the Iheya Ridge, the Okinawa Trough. JAMSTECTR Deepsea Res., **6**: 145-156.

Ohta, S. and Laubier, L., 1987, Deep biological communities in the subductionzone of Japan from bottom photographs taken during Nautile dives in the Kaiko project. Earth Planet. Sci. Lett., **83**: 329-342.

Okutani, T. and Egawa, K., 1985, The first underwater observation on living habitat and thanatocoenosis of *Calyptogena soyoae* in bathyal depth of Sagami Bay. Venus (Jpn. J. Malac.), **44**: 285-288.

Onboard scientists of the BIOACCESS Cruise, 1997, Cruise report of the BIOACCESS Cruise '96 in the Manus Basin. JAMSTEC, p.241.

Ono, K., Ito, K., Hasegawa, I., Ichikawa, K., Iizuka, t., Kakuta, T. And Suzuki, H., 1978, Explosion seismic studies in south Kyushu, especially around the Sakurajima volcano. J. Phys. Earth, **26**: S309-S319.

Ossaka, J., Hirabayashi, J., Nogami, K., Kurosaki, M. and Hashimoto, J., 1992, Variation of chemical composition of volcanic gases from the northern part of Kagoshima Bay. *Proc.*

JAMSTEC Symp. Deep Sea Res. **8**: 75-80.

Otsuka, K., Kagami, H., Honza, E. and Nasu, N., 1973, Submarine slumping as a cause of turbidity currents in Sagami Bay. Kaiyou Kagaku, **5**: 446-452.

Parkes, R.J. and Taylor, J., 1983, The relationship between fatty acid distributions and bacterial respiratory types in contemporary marine sediments. Estuarine Coastal Shelf Sci., **16**: 173-189.

Pearce, J. A., 1983, Role of the sub–continental lithosphere in magma genesis at active continental margins. In *Continental basalts and mantol xenoliths*. eds. Hawkesworth, C. J. and Norry M. J., Shiva, Nantwich, pp. 230-249.

Perry, G. J., Volkman, J. K., Johns, R. B. and Bavor Jr., H. J., 1979, Fatty acids of bacterial origin in contemporary marine sediments. Geocnem. Cosmochem. Acta, **43**: 1715-1725.

Prahl, F.G., Eglinton, G., Corner, E.D.S., O'Hara, S.C.M. and Forsberg, T.E.V., 1984, Changes in plant lipids during passage the gut of *Calanus*. Journal of the Marine Biological Assocoation of the U.K., **64**: 317-334.

Rajendran, N., Matsuda, O., Imamura, N. and Urushigawa, Y., 1992, Variation in microbial biomass and community structure in sediments of eutrophic bays as determined by phospholipid ester-linked fatty acids. Appl. Environ. Microbiol., **58**: 562-571.

Rajendran, N., Matsuda, O., Urushigawa, Y., and Simidu, U., 1994, Characterization of microbial community structure in the surface sediment of Osaka Bay, Japan, by phospholipid fatty acid analysis. Appl. Environ. Microbiol., **60**: 248-257.

Robinson, N., Cranwell, P.A., Finlay, B.J. and Eglinton, G., 1984, Lipids of aquatic organisms as potential contributors to lacstrine sediments. Org. Geochem., 6: 143-152.

Roser, B.P. and Korsch, R.J., 1986. Determination of tectonic setting of sandstone–mudstone suites using SiO_2 content and K_2O/Na_2O ratio. J. Geol., 94: 635-650.

Sakai, H., Gamo, T., Endow, K., Ishibashi, J., Ishizuka, T., Yanagisawa, F., Kusakabe, M., Akagi, T., Igarashi, G. and Ohta, S., 1987, Geochemical study of the bathyal seep communities at the Hatsushima site, Sagami Bay, Central Japan. Geochem. J., **21**: 227-236.

Sakai, H., Gamo, T., Kim, E.-S., Shitashima, K., Yanagisawa, F. and Tsutsumi, M., 1990, Unique chemistry of the hydrothermal solution in the Mid-Okinawa Trough backarc basin. Geoph. Res. Lett., **17**: 2133-2136.

Sakamoto, H., 1985, The distribution of mercury, arsenic, and antimony in sediments of Kagoshima Bay. Bull. Chem. Soc. Jpn., **58**: 580-587.

Sakamoto, H., Tomiyasu, T. and Yonehara, N., 1997, The contents and distributions of copper, zinc, cadmium and lead in sediments of Kagoshima Bay. *Rep. Fac. Sci. Kagoshima Univ.* **30**: 71-83.

Sakata, S., 1997, Hydrogen and carbon isotopic composition of methane as evidence for biogenic origin of natural gases from the Green Tuff Basin, Japan. Org. Geochem., **26**: 399-407.

Sakata, S., Suzuki, N. and Kaneko, N., 1988, A biomarker study of petroleum from the Neogene Tertiary sedimentary basins in northeast Japan. *Geochem.J.* **22**: 89-105.

Sato, T., 1986, Kuroko ore. In *Formation of Japan Islands*, Eds. Taira, A. and Nakamura, K., Iwanami, Tokyo, pp. 192-200.

Schoell, M., 1988, Multiple origins of methane in the Earth. Chem. Geol., **71**: 1-10.

Scott, L. T., 1982, Thermal rearrengements of aromatic compounds. Acc. Chem. Res., **15**: 52-58.

Scott, S. D., 1997, Submarine hydrothermal systems and deposits, In Geochemistry of hydrothermal ore deposits, third edition, ed., Barnes, H. L., John Wiley and Sons, New York, pp.797-875.

Seifert, W. K. and Moldowan, J. M., 1978, Applications of steranes, terpanes and monoaromatics to the maturation, migration and source of cruide oils, Geochem. Cosmochem. Acta, **42**: 77-95.

Shitashima, K., Gamo, T., Okamura, K. and Ishibashi, J., 1997, Trace elements at the Manus Basin, Papia New Guinea. JAMSTEC J. Deep Sea Res., **13**, 249-255.

Simoneit, B. R. T., 1994, Lipid/bitumen maturation by hydrothermal activity in sediments of Middle Valley, Leg 139. *Proc. ODP, Scientific Results* (M. J. MOTTL, E. E. DAVIS, A. T. FISHER and J. F. SLACK eds.), **139**: 447-465.

Simoneit, B.R.T. and Lonsdale, P.F., 1982, Hydrothermal petroleum in mineralized mounds at the seabed of Guaymas Basin. *Nature* **295**: 198-202.

Simoneit, B. R. T., Mazurek, M. A., Brenner, S., Crisp, P. T. and Kaplan, I. R., 1979, Organic geochemistry of recent sediments from Guaymas Basin, Gulf of California. Deep-Sea Res., **26A**: 879-891.

Simoneit, B. R. T. and Philp, R. P., 1982, Organic geochemistry of lipids and kerogen and the effects of basalt intrusions on unconsolidated oceanic sediments: Sites 477, 478, and 481, Guaymas Basin, Gulf of California. Init. Repts. DSDP, **64**: 883-904.

Simoneit, B. R. T., Kawka, O. E. and Brault, M., 1988, Origin of gases and condensates in the Guaymas Basin hydrothermal sytem (Gulf of California). Chem. Geol., **71**: 169-182.

Simoneit, B. R. T., 1993, Hydrothermal alteration of organic matter in marine and terrestrial systems. In *Organic Geochemistry*, eds., Engel, M. H. and Macko, S. M., Plenum Press, New York, 397-418.

Soh, W., Pickering, K., Taira, A. and Tokuyama, H., 1991, Basin evolution in the arc-arc Izu collision zone, Mio–Pliocene Miura Group, Central Japan. Geol. Soc. London, **148**: 317-330.

Suess, E., Carson, B., Ritger, S., Moore, J. C., Kulm, L. D. and Cochrane, G. R., 1985, Biological communities at a vent site along the subduction zone off Oregon. Bull. Biol. Soc. Wash., **6**: 475-484.

Taguchi, K., 1968, Geochemical significance of n-alkane, porphyrin pigments and polycyclic aromatics in stratigraphic correlation of source rocks. J. Geol. Soc. Jpn. **74**: 385-398.

Taira, A., Tokuyama, H. and Soh, W., 1989, Acceretion tectonics and evolution of Japan. In *Evolution of PacificOcean Margins*. ed., Ben-Avraham, Z., Oxford Univ. Press, New York, pp. 100-123.

Takada, H., 1993. Hydrocarbons in sediment. Gekkan Kaiyou, **25**: 24-29.

Takahashi, M., 1997. The structure of high level crustal magmatic plumbing system benearth the Quaternary arc volcanoes in Japan Islands. Bull. Volcanol. Soc. Jpn., 42: S175-S187.

Tanimura, S., Date, J., Takahashi, T. and Ohmoto, H., 1983, Geological, paleontological, and tectonic studies: Geologic setting of the Kuroko deposits, Japan: Part II. Stratigraphy and structure of the Hokuroku district. In: The Kuroko and related volcanogenic massive sulfide deposits, eds., Ohmoto, H., and Skinner, B. J., Econ. Geol. Monograph **5**: 24-39.

Taylor, B., Crook, K. W. A., Sinton, J. and Petersen, L., 1991, Manus Basin, Papua New Guinea, In *Pacific Seafloor Atlas*, Hawaii Institute of Geophysics, Sheets 1-7.

Taylor, J. and Parkes, R. J., 1983, The cellular fatty acids of the sulphate reducing bactria, *Desulfobacter sp.*, *Desulfobulbus sp.*, and *Desulfovibrio desulfuricans*. J. Gen. Microbiol., **129**: 3303-3309.

Taylor, J. and Parkes, R. J., 1985, Identifying differnt populations of sulphate reducing bacteria within marine sediment system, using fatty acid biomarkers. J. Gen. Microbiol., **131**: 631-642.

Thode, H. G., 1988, Sulphur Isotopes in Nature and the Environment: An Overview. In *SCOPE43 Stable Isotopes: NAtural and Anthropogenic Sulphur in the Environment*, H. R. Krouse and V. A. Grinenko, John Wiley & Sons, Chichester, 7-26.

Tissot, B. P. and Welte, D. H., 1984, *Petroleum formation and occurrence: A new approach to oil and gas exploration*. 2Nd ed., Springer-Verlag, Berlin.

Tokuyama, H., 1996, 3D structure and history of teh Kanto Earthquake in 1923, Report of the grant in aid for scientific study, No.06405003, Ocean Res. Inst. Univ. Tokyo, p. 60.

Tsugaru, R., Tamaki, Y., Sako, M., Kimura, M. and Shimamura, K., 1991, Report on DELP 1988 Cruise in the Okinawa Trough Part 4. Preliminary report on the sediment samples. Bull. Earthquake Res. Inst. Univ. Tokyo, **66**: 71-89.

Tsunogai, U., Ishibashi, J., Wakita, H., Gamo, T., Masuzawa, T. and Nakatsuka, T., 1994, Source of "cold seepage at the off Hatsushima Island, Sagami Bay: a preliminary report of the Dive 921 of "Shinkai 2000". JAMSTEC J. Deep Sea Res., **10**: 395-403.

Tsunogai, U., Ishibashi, J., Wakita, H., Gamo, T., Iizasa, K., Fiske, R. S. and Naka, J., 1995, Hydrothermal activity in the Kita-Bayonnaise submarine caldera, Izu-Bonin Arc. JAMSTEC J. Deep Sea Res., **11**: 333-339.

Tsunogai, U., Ishibashi, J., Wakita, H., Gamo, T., Masuzawa, T., Nakatsuka, T., Nojiri, Y. and Nakamura, T., 1996, Fresh water seepage and pore water recycling on the seafloor: Sagami Trough Subduction Zone, Japan. Earth Planet. Sci. Lett., **138**: 157-168.

Tsuyuki, T., 1969, Geological study of hot springs in Kyushu, Japan. (5) Some hot springs

in the Kagoshima Graben, with special reference to thermal water reservoir. *Rep. Fac. Sci. Kagoshima Univ. Earth Science and Biology* **2**: 85-101.

Tufa, W., 1990, Modern hydrothermal activity, formation of complex massive sulfide deposits and associated vent communities in the Manus Back Arc Basin (Bismark Sea, Papua New Guinea). Mitteilung der oesterreichen geologischen Gesellschalt, **82**: 183-210.

Utashiro, S. and Iwabuchi, Y., 1971, The submarine topography and geological structure of Sagami Bay, south coast of Honshu, Japan. Chigaku Zasshi, **80**: 77-88.

Uzaki, M., Yamada, K. and Ishiwatari, R., 1993, Carbon istope evidence for oil-pollution in long chain normal alkanes in Tokyo Bay sediments. Geochim. J., **27**: 385-389.

Van Vleet, E. S. and Quinn, J. G., 1979, Early diagenesis of fatty acids and isoprenoid alchols in estuarine and coastal sediments. Geochim. Cosmochim. Acta, **43**: 289-303.

Volkman, J.K., 1986, A review of sterol markers for marine and terrigenous organic matter. Organic Geochemistry, **9**: 83-99.

Von Damm, K. L., 1995, Controls on the chemistry and temporal variability of seafloor hydrothermal fluids. In *Seafloor hydrothermal systems–Physical, chemical, biological and geological interactions*, S. Humphris, L. Mullineaux, R. Zierenberg and R. Thomson, **91**, Am. Geophys. Un., Washington, D.C., 222-247.

Wakita, H., Sano, Y., Urabe, A. and Nakamura Y., 1990, Origin of methane-rich natural gas in Japan: formation of gas fields due to large-scale submarine volcanism. Appl. Geochem., **5**: 263-278.

White, D. C., 1983, Analysis of microorganisms in terms of quantity and activity in natural environments. Microbesn in their natural environments. Soc. Gen. Microbiol. Symp., **34**: 37-66.

White, D. C., Bobbie, R. J., King, J. D., Nickels, J. S. and Morrison, S. J., 1979a, Biochemical measurements of microbial biomass and community structure from environmental samples. In Native Aquatic Bacteria: Enumeration, Activity, and Ecology. Eds. Costerton, J. W. and Colwell, R. R., ASTM **695**: 69-81.

White, D. C., Davis, W. M., Nickels, J. S., King, J. D. and Bobbie, R. J., 1979b, Determination of the sedimentary microbial biomass by extractible lipid phospate. Oecologia, **40**: 51-62.

White, D. C., Smith, G. A. and Stanton, G. R., 1984, Biomass, community structure and metabolic activity of the microbiota in Antarctic benthic marine sediments and sponge spicule mats. Antarct. J. U.S., **29**: 125-126.

Yamada, Y. and Uchida, T., 1997, Characteristics of hydrothermal alteration and secondary porosities in volcanic rock reservoirs, the Katakai gas field. J. Jpn Assoc. Petrol. Technol. **62**: 311-320.

Yamanaka, T., Mizota, C., Murae, T. amd Hashimoto, J., 1999, A currently forming petroleum associated with hydrothermal mineralization in a submarine caldera,

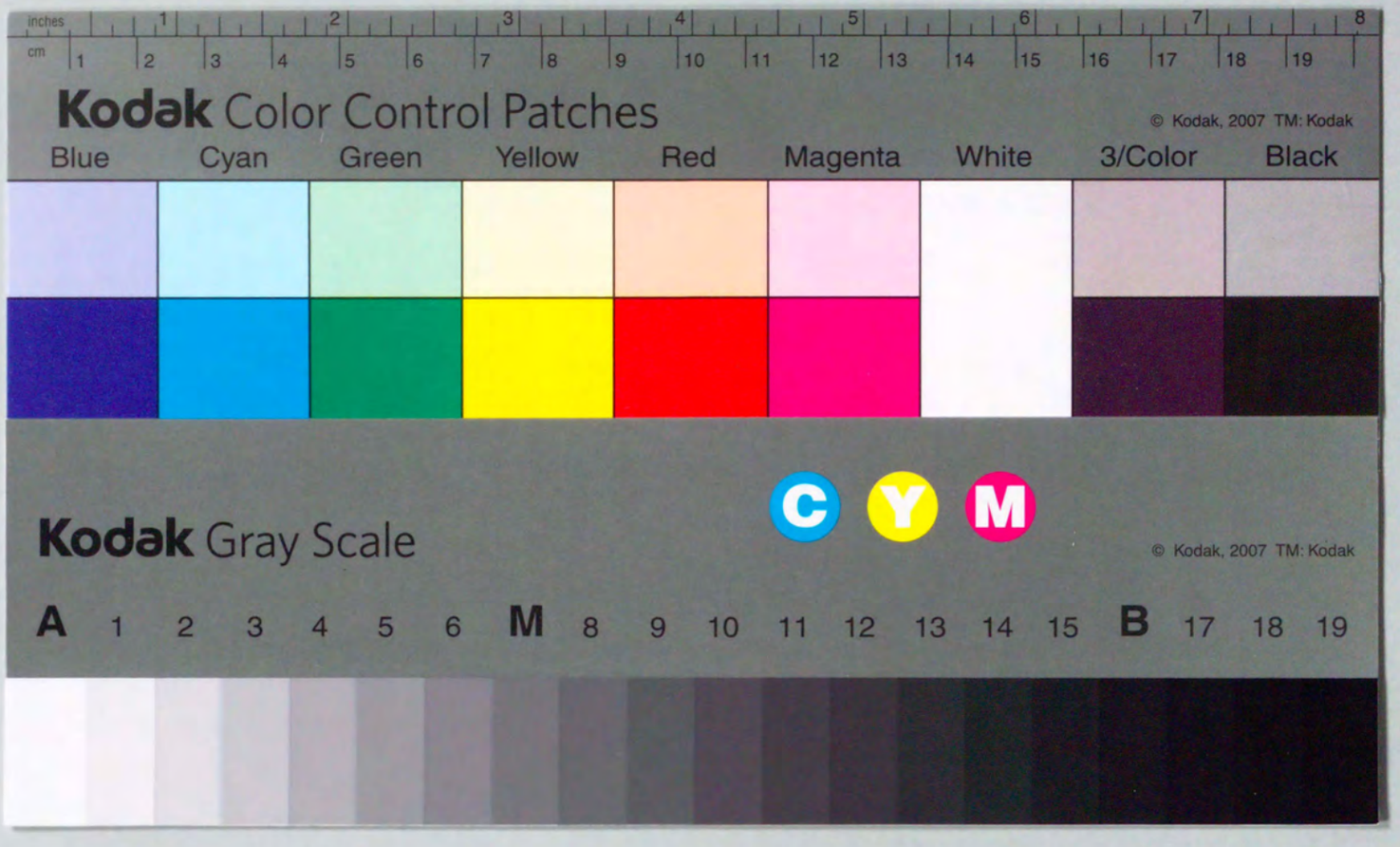
Kagoshima Bay, Japan. Geochem. J., **33** (submitted).

Yoshida, N. and Tsukahara, H., 1991, $^{14}C/^{12}C$ and $^{13}C/^{12}C$ in the shell of *Calyptogena soyoae* from the subduction zone Sagami Bay and fluid flow from the deep part of the sea floor. JAMSTECTR Deep Sea Res., **7**: 25-31.

Youngblood, W. W. and Blumer, M., 1975, Polycyclic aromatic hydrocarbons in the environment: homologus series in soils and recent marine sediments. Geochim. Cosmochim. Acta, **39**: 1303-1314.

Yuasa, M., Murakami, F., Saito, E. and Watanabe, K., 1991, Submarine topography of seamounts on the volcanic front of the Izu-Ogasawara (Bonnin) arc. Geol. Sur. Jpn., **42**: 703-743.

Yuasa, M., Fujiwara, Y., Horii, Y., Ishibashi, J., Isizuka, O., Koyama, S., Higashide, Y., Uematshu, K. and Yamanaka, T., 1998, Geological and biological phenomena involving with seafloor hydrothermal activity in Myojin Knoll, northern Izu-Ogasawara arc, Abst. Shinkai Symp., JAMSTEC, Tokyo, 63-64.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