Organic geochemical study of natural gases
from major gas fields in Japan

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Abstract: Light hydrocarbons from several natural gas fields in Japan were measured, including neopentane which has been rarely measured. Logarithms of ethane/propane and neopentane/isopentane, ethane/propane and neopentane/isobutane, and neopentane/isopentane and neopentane/isobutane ratios show good straight line correlations, respectively. These correlations can be explained by decomposition of these hydrocarbons due to hydrogen abstraction. It is concluded that the decomposition process of the hydrocarbons is the major determining factor for the hydrocarbon composition of natural gases.

Effect of rock types on the fractionation of light hydrocarbons in natural gases during migration through rocks was investigated. For this purpose the retention times of hydrocarbons on gas chromatographic columns packed with various rock and mineral samples were measured. Hydrocarbons used for this experiment were CH_4, C_2H_6, C_3H_8, iso-C_4H_{10}, n-C_4H_{10}, iso-C_5H_{12} and n-C_5H_{12}. The fractionation occurred with expandable clay minerals or zeolites. The order of retention times depends on the species of clay minerals or zeolites. When montmorillonite, halloysite, vermiculite and mordenite were used, the order was $CH_4 < C_2H_6 < C_3H_8 < iso\text{-}C_4H_{10} < n\text{-}C_4H_{10} < iso\text{-}C_5H_{12} < n\text{-}C_5H_{12}$. When clinoptilolite was used, the order was $CH_4 < iso\text{-}C_4H_{10} < C_2H_6 < iso\text{-}C_5H_{12} < C_3H_8 < n\text{-}C_4H_{10}$. The fractionation became larger with aging of the mineral samples. When the samples were not aged, only a small fractionation was observed. These results show that the dehydrated state of the interlayer spaces of clay minerals or pore spaces of zeolites plays an important role in fractionation. Furthermore, these results suggest that the large fractionation by clay minerals or zeolites does not occur under normal subsurface conditions where these minerals are hydrated.

Carbon isotopic ratios of methane ($\delta^{13}C(CH_4)$) were measured for dissolved-in-water type natural gases from several gas fields in Japan. Some samples have relatively low $\delta^{13}C(CH_4)$ values. This indicates that they are of biogenic origin as has been suggested by previous researchers. However, several samples from Fukushima, Shizuoka, Miyazaki and Kagoshima prefectures have relatively high $\delta^{13}C(CH_4)$ values, which cannot be of biogenic origin, but of thermogenic origin. This is the first evidence to confirm the occurrence of dissolved-in-water type gas of thermogenic origin in Japan.

Carbon isotopic ratios of methane, ethane and propane ($\delta^{13}C(CH_4)$, $\delta^{13}C(C_2H_6)$ and $\delta^{13}C(C_3H_8)$, respectively) were analyzed for oil field gases from Niigata and Akita in Japan. A strong correlation between $\delta^{13}C(C_2H_6)$ and $\delta^{13}C(C_3H_8)$ was observed. This relation is well explained by a kinetic theory proposed by Chung *et al.* (1988). On the other hand, only a weak correlation was observed between $\delta^{13}C(CH_4)$ and $\delta^{13}C(C_2H_6)$. The weak correlation is inferred to be due to a mixing of biogenic gas that has low $\delta^{13}C(CH_4)$. Furthermore, the mixing ratios of thermogenic gas and biogenic gas can be calculated from the values of $\delta^{13}C(CH_4)$, $\delta^{13}C(C_2H_6)$ and $\delta^{13}C(C_3H_8)$. It is found that almost all the oil field gases in Akita and Niigata are mixtures of thermogenic and biogenic gases.

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Dissolved-in-water type gas
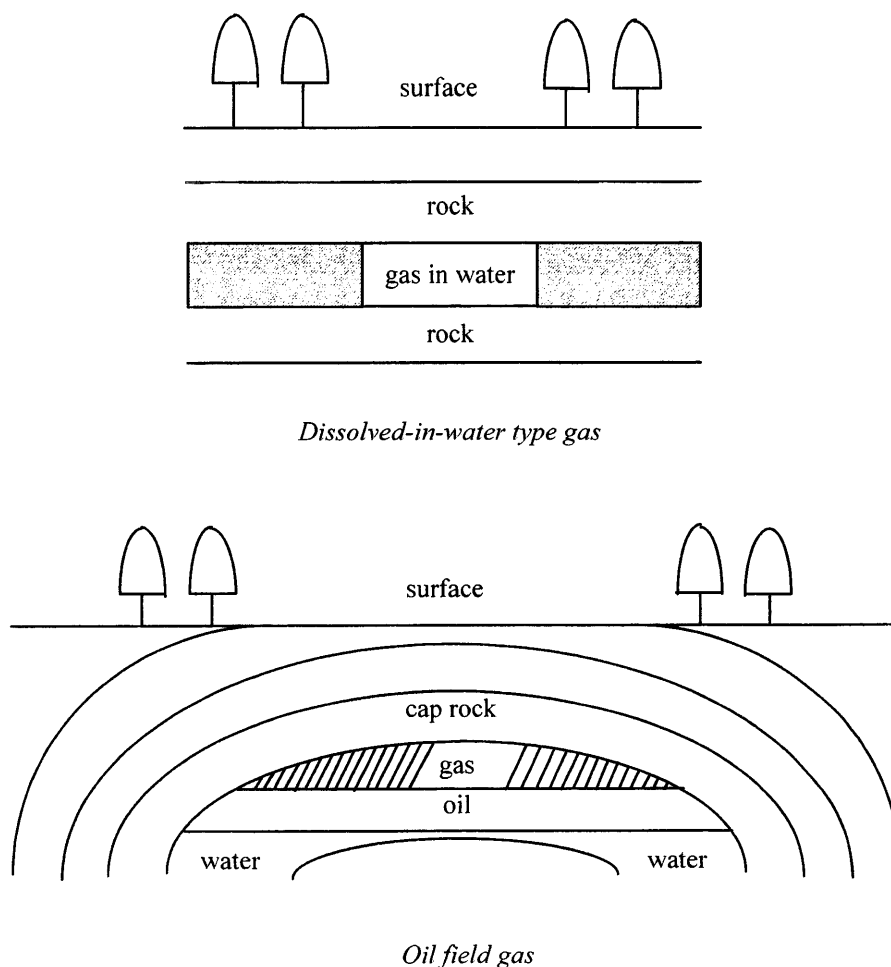
Oil field gas

Fig. 1   Types of gas fields.

1.   Introduction

1.1   Types of natural gases

Natural gases in gas fields are classified into two types by their origins; biogenic and thermogenic gases (Fuex, 1977; Schoell, 1983). The biogenic gases are produced from CO_2 in sediments by bacterial reduction or from organic matter in sediments by bacterial decomposition. The thermogenic gases are produced from kerogen by thermal decomposition in sediments. The mixing of the two types could occur in sediments and reservoir rocks. Further, existence of magmatic gas has been discussed (Welhan and Craig, 1981; Wakita and Sano, 1983).

Another classification of natural gases is based on their occurrences; dissolved-in-water type gas and oil field gas (Sugisaki, 1964). Dissolved-in-water type gas is defined as a gas which is dissolved in underground water. Oil field gas is defined as a gas which is related to the oil field in occurrence (Fig. 1).

1.2   Factors affecting hydrocarbon compositions

The main components of natural gas are hydrocar-

bons. The hydrocarbon compositions are an important parameter for gas correlation. The known primary factors affecting hydrocarbon compositions are origin and maturity. Secondary factors are bacterial degradation or migration in sediments.

As for origin, thermogenic gas usually contains many nonmethane hydrocarbons, while biogenic gas contains little nonmethane hydrocarbons (Schoell, 1983; Noble and Henk, 1998). The trace nonmethane hydrocarbons contained in biogenic gas are known to be of thermogenic origin, because of the fact that bacteria produces very little nonmethane hydrocarbons (Davis and Squires; 1954).

It is known that the hydrocarbon composition of thermogenic gas depends on maturity of the gas and types of kerogen (Rice, 1983; Schoell, 1983; Chen *et al.*, 2000). High maturity thermogenic gas shows a high methane/nonmethane hydrocarbon ratio as a result of cracking of the C-C bonds in the larger hydrocarbon molecules. Further, Heroux *et al.* (1979), and Connan   and   Cassou   (1980)   showed   the isobutane/n-butane ratio depends on maturity. The ratio is high in the case where maturity is high. Kato (1989) showed that isobutane /n-butane ratios in the
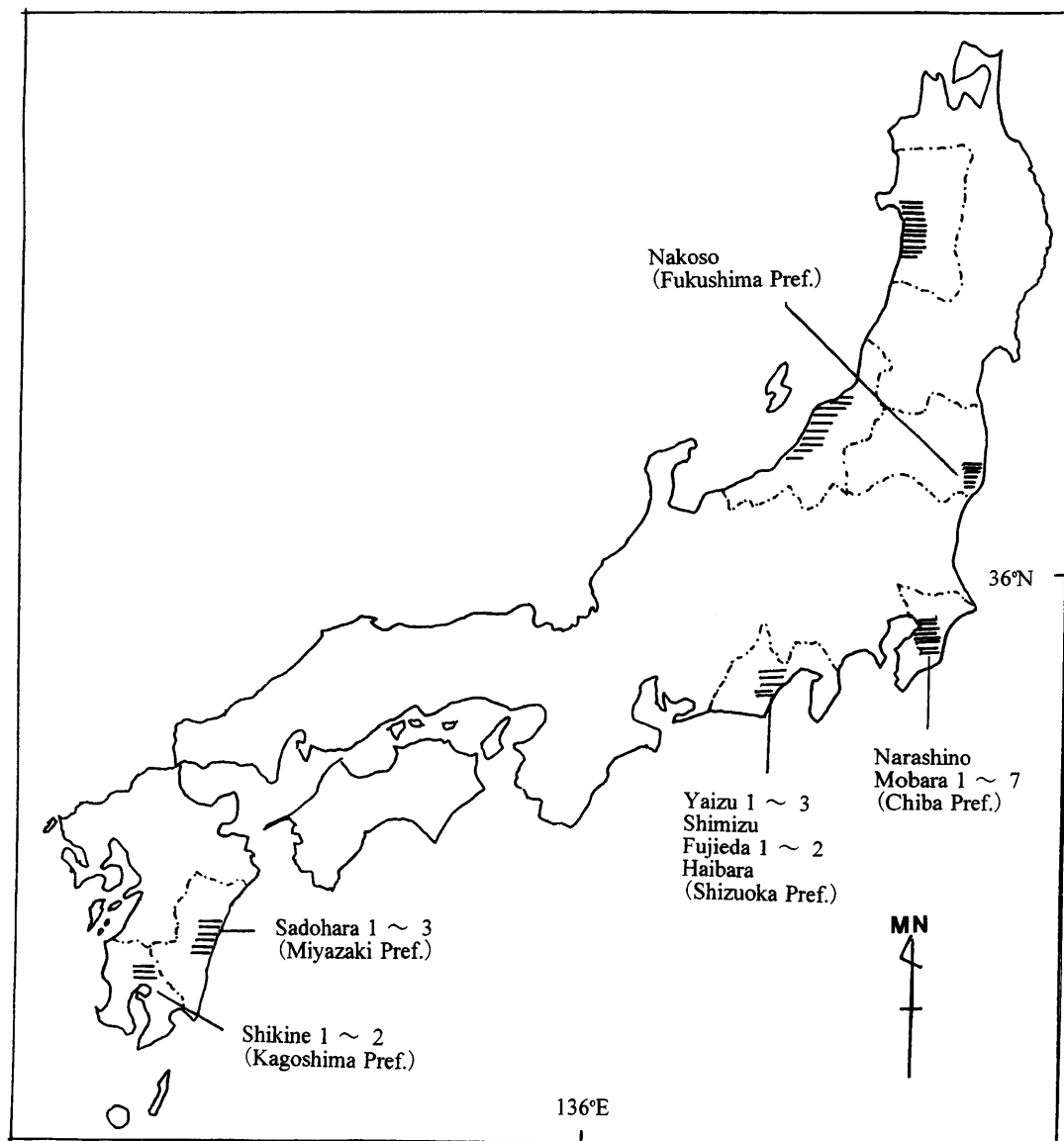
Fig. 2-1 Sampling sites of dissolved-in-water type gases.

gases from Niigata correlate with $\delta^{13}C(CH_4)$, and suggested that the ratios can be used as a maturity parameter. For the kerogen type, it is known that gases from type Ⅲ kerogen show a relatively low concentration of nonmethane hydrocarbon (Chen *et al,* 2000). As for gases in Japan, Yonetani (1986) showed the isobutane/*n*-butane ratio depends on the type of kerogen, but the reason is unclear.

However, factors affecting hydrocarbon compositions are still only partially known. Therefore, hydrocarbon compositions in natural gases were measured and factors affecting hydrocarbon compositions are investigated in this study analyzing their concentrations in gases from major oil and gas fields in Akita, Niigata, Fukushima, Chiba, Shizuoka, Miyazaki and Kagoshima in Japan.

1.3 Compositional change due to migration

Hydrocarbon compositions of natural gases are an important parameter for the correlation of gases in origin and maturity. However, the correlation can not be made easily because of possible changes in the natural gas composition during migration in sediments from source rocks to reservoir rocks. Leythaeuser *et al.* (1979, 1980, 1982, 1983) and Whelan *et al.* (1984) analyzed hydrocarbon compositions of adsorbed gases in rocks above the gas deposit, and calculated diffusion coefficients for each hydrocarbon. Kross and Schaefer (1987), Kross (1988), and Kross and Leythaeuser (1988) calculated diffusion coefficients by simulation experiments using rock samples saturated with water. Whiticar (1994) reported that higher molecular weight hydrocarbons show lower diffusion coefficients. However, in these simulations, other factors also affected the fractionation of the hydrocarbon composi-

Yabase 1 ~ 6
Sarukawa 1 ~ 4
Nishioogata 1 ~ 2
Fukumezawa
Yurihara 1 ~ 2
(Akita Pref.)

Higashiniigata 1 ~ 5
Minaminagaoka
Katakai
Yoshii
Higashikasiwazaki
Kubiki 1 ~ 3
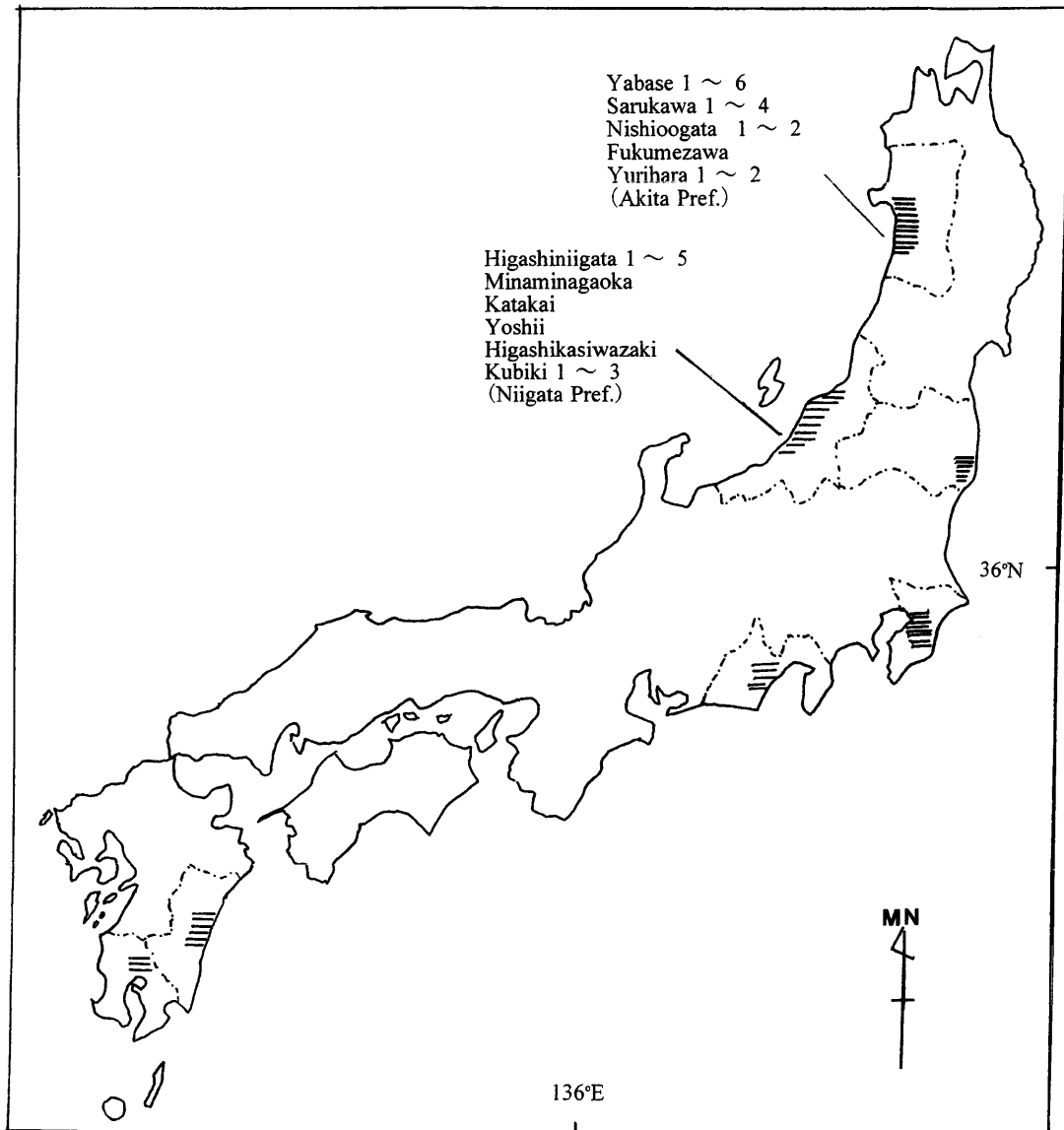(Niigata Pref.)

36°N

MN

136°E

Fig. 2-2   Sampling sites of oil field gases.

tions during migration. These factors are existence of water, porosity, permeability, rock type etc. To uncover the general rule for the hydrocarbon fractionation in rocks, the effect of each factor must be known. Since little is known on the effect of rock type, simulation experiments using gas chromatography were performed in this study.

1.4   Origins of dissolved-in-water type gases

Natural gas of dissolved-in-water type is widely found in Japan. Several geological studies have been done to explain the formation processes of the dissolved-in-water type gas deposits (e.g. Ijima, 1959; Sugisaki, 1964; Marsden and Kawai, 1965). However there are few reports concerning the origin of dissolved-in-water type gas.

It is known that thermogenic gases often contain high concentrations of nonmethane hydrocarbons and

show high $\delta^{13}C(CH_4)$ values (about -25 ~ -45 ‰) (Stahl, 1974; Shoell, 1983, 1988). On the other hand, biogenic gases contain little nonmethane hydrocarbons and show low $\delta^{13}C(CH_4)$ values (about -60 ~ -70 ‰) (Rice and Claypool, 1981). Mixed gases of both types have intermediate nonmethane hydrocarbon concentrations and $\delta^{13}C(CH_4)$ values. Further, it is considered that magmatic gas shows very high $\delta^{13}C(CH_4)$ value (about -15 ‰) (Welhan and Craig, 1981).

Nakai (1960) and Nakai *et al.* (1974) measured carbon and hydrogen isotopic compositions of dissolved-in-water type gases from the Niigata, Mobara, Suwa, Yamagata and Tokyo gas fields and concluded that they are of biogenic origin. Waseda and Omokawa (1988) measured carbon isotopic and chemical compositions of several dissolved-in-water type gases from the Kisakata gas field in Akita, and concluded that they are of biogenic origin with a small

mixing of thermogenic gases. In the present study, chemical and carbon isotopic studies are extended to other gas fields, and the origins of the dissolved-in-water type gases in Japan are discussed.

1.5 Carbon isotopic ratios of oil field gases

For understanding the origins of natural gases, $\delta^{13}C(CH_4)$ is usually measured. Further, maturity of thermogenic gas is estimated from $\delta^{13}C(CH_4)$ (Shoell, 1983). A few studies have been done to understand the origin and maturity of oil field gases from Niigata and Akita in Japan by using this parameter (Sakata *et al.*, 1986; Waseda and Omokawa, 1988). However as to origin, the distinction between immature thermogenic gas and mixed gas is difficult because they show similar $\delta^{13}C(CH_4)$ values. Determination of thermogenic gas maturity is difficult because $\delta^{13}C(CH_4)$ of thermogenic gases is changed by mixing of biogenic gases. To understand the origin and maturity of oil field gases, other parameters must be measured. Therefore, in this study $\delta^{13}C(C_2H_6)$ and $\delta^{13}C(C_3H_8)$ of oil field gases in Niigata and Akita were measured and the factors determining those values were evaluated.

2. Factor affecting hydrocarbon compositions of natural gases.

2.1 Experiments
Samples

Oil field gas samples were collected from oil and gas fields in Akita and Niigata (Fig. 2-1), and dissolved-in-water type gas samples were collected from gas fields in Fukushima, Chiba, Shizuoka Miyazaki and Kagoshima (Fig. 2-2) by a water-displacement method using a saturated sodium chloride solution (Fig. 3). The samples were stored in Pyrex glass bottles or beer bottles which were opened just before the analysis.

Analysis

The oil field gases were measured in the range of methane to *n*-hexane. A Hewlett Packard HP5890A

gas chromatograph (carrier gas: He) equipped with a Spelco column (SPB-1, fused silica capillary, length: 60 m, inside diameter 0.32 mm) was used (Table 1).

For dissolved-in-water type gases, the measured hydrocarbons are in the range of methane to *n*-pentane. Methane was measured by a Shimadzu 8A gas chromatograph (detector: TCD, carrier gas: argon, column: packed with molecular sieve 5A, column length: 3 m, injector and detector temperature: 60 ℃, column temperature: 50 ℃). Other hydrocarbons were measured by a Hewlett Packard 5890A gas chromatograph (detector: FID, carrier gas: helium, column: packed with silica gel, column length: 2 m, injection and detector temperature: 200 ℃, column temperature: initially 70 ℃ then increased to 120 ℃ at a rate of 1 ℃ /min.) (Table 1).
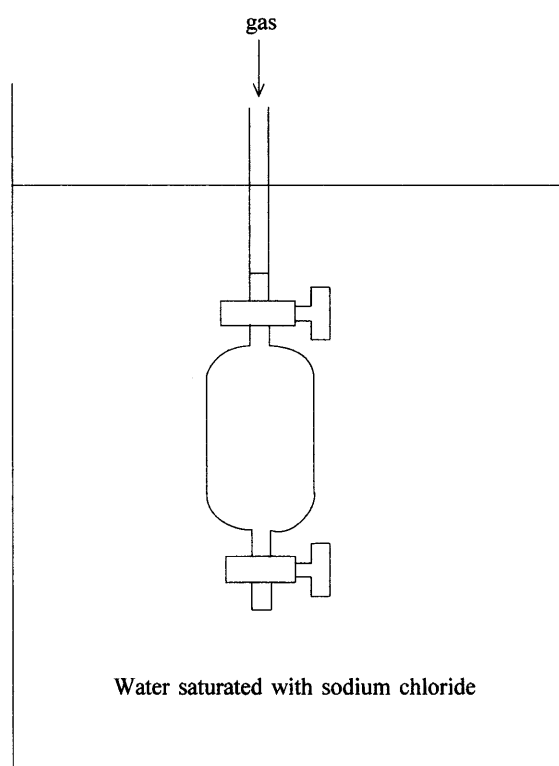
gas
↓

Water saturated with sodium chloride

Fig. 3   Sampling tool.

Table 1   Conditions for gas chromatographic analysis.

Gas field type	Molecule	Gas chromatograph	Column type	Column	Carrier	Column temperature
Oil field gas	CH_4, C_2H_6, C_3H_8, iso-C_4H_{10}, *n*-C_4H_{10}, neo-C_5H_{12}, iso-C_5H_{12}, *n*-C_5H_{12}, 2,2-DMB, 2,3-DMB, 2-MP, 3-MP, *n*-C_6H_{12}	Hewlett Packard HP5890A	capillary	Spelco SPB-1	He	40°C
Dissolved-in-water type ga:	CH_4	Shimadzu 8A	packed	Molecular sieve 5/ Ar		50°C
	C_2H_6, C_3H_8, iso-C_4H_{10}, *n*-C_4H_1 neo-C_5H_{12}, iso-C_5H_{12}, *n*-C_5H_{12},	Hewlett Packard HP5890A	packed	Silica gel	He	70°C then increased to 120°C at a rate of 1°C/min.

2,2-DMB: 2,2-dimetylbutane, 2,3-DMB: 2,3-dimethylbutane, 2-MP: 2-methylpentane, 3-MP: 3-methylpentane

2.2 Results

A gas chromatogram of an oil field gas (Sarukawa-3) is shown in Fig. 4. Gas chromatograms of dissolved-in-water type gas (Yaizu-2) are shown in

Figs. 5 and 6. For the oil field gas samples, CH_4 is in the range of 55.7 ~ 95.9 %. CH_4 is the main component. C_2H_6, C_3H_8, iso-C_4H_{10}, n-C_4H_{10}, neo-C_5H_{12}, iso-C_5H_{12} and n-C_5H_{12} are in the range of
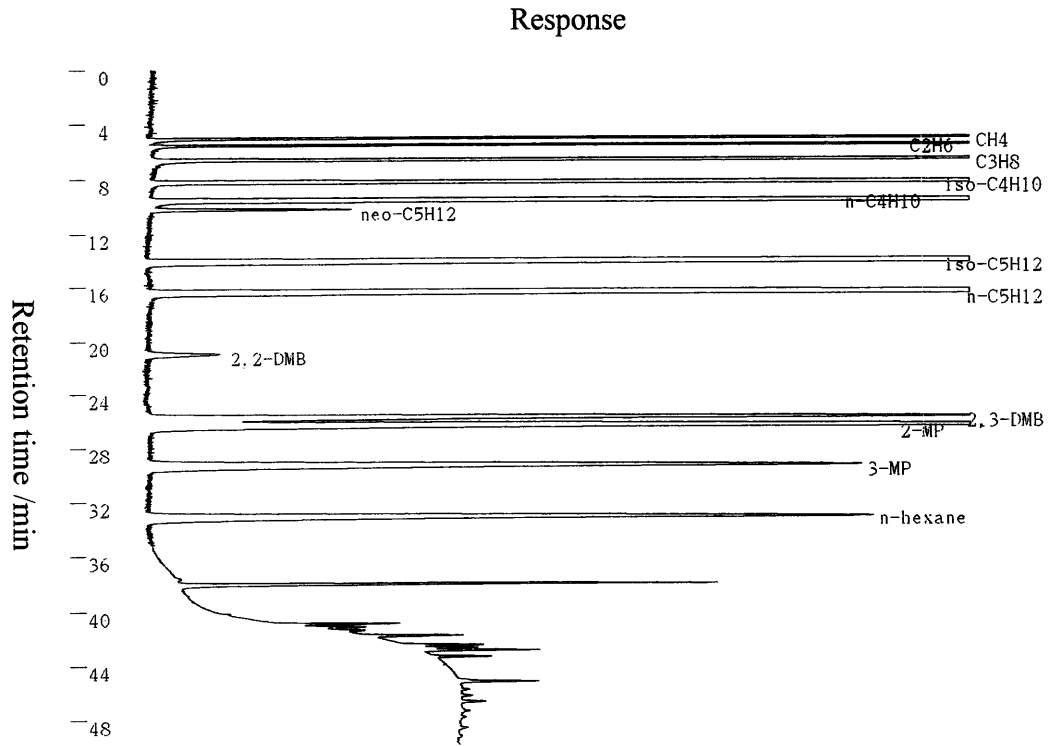

Fig. 4   Gas chromatogram of oil field gas (Sarukawa-3).
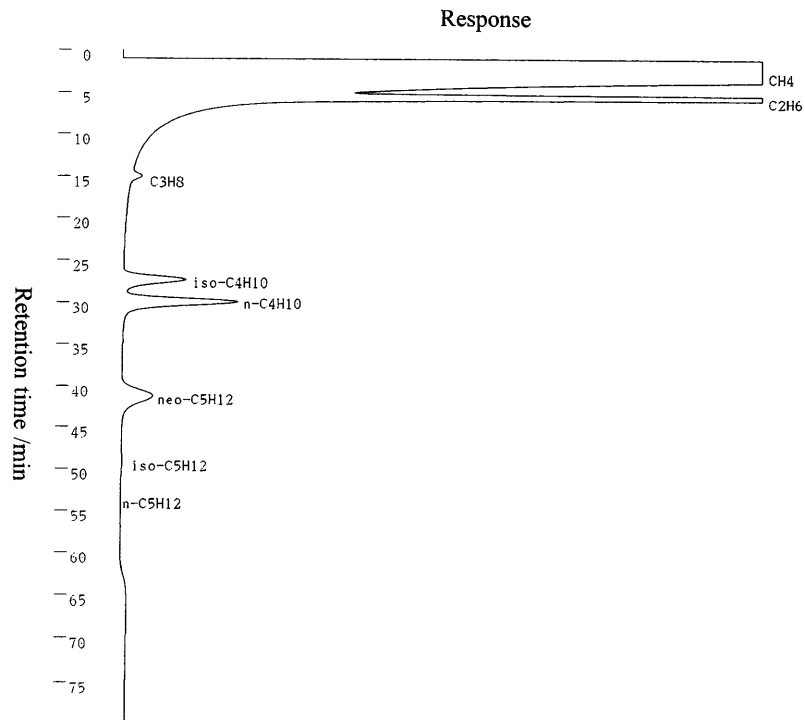

Fig. 5   Gas chromatogram of dissolved-in-water type gas (Yaizu-2).

0.83 ～ 15.5 %, 0.02 ～ 15.7 %, 0.03 ～ 4.49 %, 0.01 ～ 7.55 %, 16 ～ 74 ppm, 40 ～ 21300 ppm and 8 ～ 15600 ppm, respectively as shown in Table 2. They show relatively high concentrations. The range for

2,2-dimethylbutane (2,2-DMB), 2,3-dimethylbutane (2,3-DMB), 2-methylpentane (2-MP), 3-methylpentane (3-MP) and n-C_6H_{12} is 23 ～ 85 ppm, 69 ～ 1230 ppm, 120 ～ 1760 ppm, 70 ～ 1170
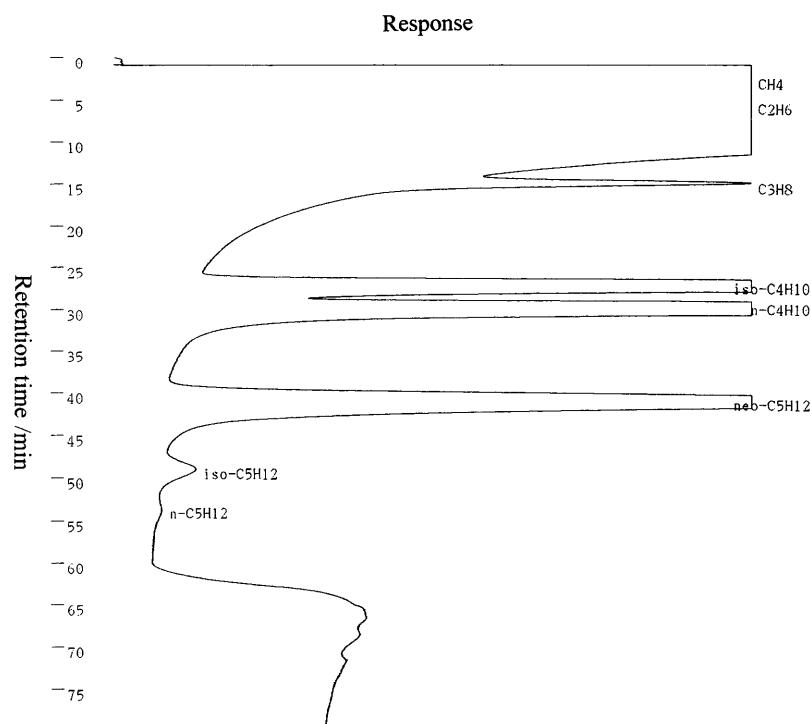

Fig. 6 Gas chromatogram of dissolved-in-water type gas (Yaizu-2, enlarged).

Table 2   Oil field gases and their hydrocarbon compositions.

No.	Gas field or gas sign	CH_4 /%	C_2H_6 /%	C_3H_8 /%	iso-C_4H_{10} /%	n-C_4H_{10} /%	neo-C_5H_{12} /ppm	iso-C_5H_{12} /ppm	n-C_5H_{12} /ppm
23	Yabase-1*	75.3	5.23	6.98	1.36	2.36	59	5010	2730
24	Yabase-2*	72.1	9.20	5.99	0.96	2.25	56	8390	7230
25	Yabase-3*	79.5	8.56	3.71	0.56	1.02	34	3000	2420
26	Yabase-4	64.5	14.50	9.98	1.43	2.73	NM	7420	6160
27	Yabase-5	61.6	14.50	13.90	1.48	3.23	NM	8990	9420
28	Yabase-6	62.1	15.50	13.10	1.41	3.01	NM	15160	4170
29	Sarukawa-1*	62.6	9.01	12.39	1.91	3.30	74	6380	4050
30	Sarukawa-2*	83.6	5.64	3.01	0.37	0.67	16	2170	1360
31	Sarukawa-3*	63.7	8.01	7.30	1.09	2.24	43	5340	3930
32	Sarukawa-4	69.6	9.36	10.30	2.43	4.15	NM	6050	4280
33	Nishioogata-1*	76.2	8.19	4.24	0.80	1.35	58	6370	3940
34	Nishioogata-2	74.4	10.90	4.80	0.63	0.80	NM	1550	938
35	Fukumezawa	84.8	6.51	2.25	0.26	0.37	NM	760	490
36	Yurihara-1*	77.6	9.86	4.70	0.67	0.98	36	2030	1530
37	Yurihara-2	55.7	7.91	15.70	4.49	7.55	NM	21300	15600
38	Mitsuke-1*	83.1	6.07	2.40	0.45	0.60	40	1710	1130
39	Mitsuke-2*	84.6	5.85	2.15	0.42	0.52	43	1480	780
40	Higashiniigata-1*	87.4	4.51	1.89	0.41	0.53	34	1830	1110
41	Higashiniigata-2*	84.6	6.21	2.44	0.54	0.72	50	2780	1780
42	Higashiniigata-3*	78.2	4.79	1.63	0.40	0.46	51	1890	1110
43	Higashiniigata-4	85.5	6.75	2.58	0.52	0.57	NM	1790	1070
44	Higashiniigata-5	85.8	6.32	2.42	0.50	0.61	NM	2100	1210
45	Minaminagaoka*	80.7	4.76	1.60	0.40	0.42	41	1590	920
46	Katakai*	80.6	5.48	1.93	0.37	0.48	32	1560	1110
47	Yoshii	78.3	6.33	4.32	1.56	2.03	NM	8280	4890
48	Higashikashiwazaki*	85.4	5.03	1.97	0.45	0.52	52	1900	1180
49	Kubiki-1*	88.0	4.55	1.19	0.36	0.37	33	1720	850
50	Kubiki-2	71.2	4.33	1.17	0.24	0.24	NM	640	220
51	Kubiki-3	95.9	0.83	0.02	0.03	0.01	NM	40	8

NM not measured
* Igari (1996)

ppm and 60 ~ 1350 ppm, respectively (Table 3). For the dissolved-in-water type gas samples, CH_4 is in the range of 49.3 ~ 95.0 %. CH_4 is the main component. C_2H_6, C_3H_8, iso-C_4H_{10}, n-C_4H_{10}, neo-C_5H_{12}, iso-C_5H_{12} and n-C_5H_{12} are in the range of 14 ~ 880

ppm, nd (not detected) ~120 ppm, nd ~ 23 ppm, nd ~ 35 ppm, 0.01 ~7.0 ppm, nd ~ 5.6 ppm and nd ~ 4.5 ppm, respectively, (Table 4). They show relatively low concentrations.

Table 3   Oil field gases and their hexane isomer concentrations.

No.	Gas field or gas sign	2,2-DMB (ppm)	2,3-DMB (ppm)	2-MP (ppm)	3-MP (ppm)	n-C_6H_{12} (ppm)
23	Yabase-1	26	180	290	160	97
24	Yabase-2	84	1230	1760	1170	1350
25	Yabase-3	41	220	520	320	410
26	Yabase-4	NM	NM	NM	NM	NM
27	Yabase-5	NM	NM	NM	NM	NM
28	Yabase-6	NM	NM	NM	NM	NM
29	Sarukawa-1	31	250	420	250	230
30	Sarukawa-2	16	130	220	150	78
31	Sarukawa-3	29	340	550	350	370
32	Sarukawa-4	NM	NM	NM	NM	NM
33	Nishioogata-1	85	330	630	370	220
34	Nishioogata-2	NM	NM	NM	NM	NM
35	Fukumezawa	NM	NM	NM	NM	NM
36	Yurihara-1	23	120	240	130	210
37	Yurihara-2	NM	NM	NM	NM	NM
38	Mitsuke-1	42	110	220	130	190
39	Mitsuke-2	36	69	120	70	60
40	Higashiniigata-1	39	100	240	140	150
41	Higashiniigata-2	70	200	410	240	300
42	Higashiniigata-3	56	89	260	140	170
43	Higashiniigata-4	NM	NM	NM	NM	NM
44	Higashiniigata-5	NM	NM	NM	NM	NM
45	Minaminagaoka	47	91	210	130	180
46	Katakai	42	110	240	150	210
47	Yoshii	NM	NM	NM	NM	NM
48	Higashikashiwazaki	61	130	320	190	290
49	Kubiki-1	32	160	240	150	160
50	Kubiki-2	NM	NM	NM	NM	NM
51	Kubiki-3	NM	NM	NM	NM	NM

NM not measured

Table 4   Dissolved-in-water type gases and their hydrocarbon compositions (Igari, 1996).

No.	Gas field or gas sign	CH_4 /%	C_2H_6* /ppm	C_3H_8 /ppm	iso-C_4H_{10} /ppm	n-C_4H_{10} /ppm	neo-C_5H_{12} /ppm	iso-C_5H_{12} /ppm	n-C_5H_{12} /ppm
1 [1]	Nakoso	93.7	120	0.75	0.058	0.042	0.16	0.053	0.032
2 [1]	Nakoso	89.7	110	0.83	0.050	0.048	0.17	0.050	0.036
3	Narashino	90.8	100	0.44	0.019	0.018	0.029	0.056	0.060
4	Mobara-1	92.3	120	0.94	0.054	0.051	0.038	0.050	0.034
5	Mobara-2	91.0	110	0.20	nd	0.013	0.014	nd	nd
6	Mobara-3	92.2	120	0.59	0.015	0.022	0.014	nd	nd
7	Mobara-4	88.6	160	23.0	1.25	0.47	0.016	0.084	0.014
8	Mobara-5	90.7	70	0.22	nd	0.009	0.015	nd	nd
9	Mobara-6	85.4	80	0.54	0.038	0.15	0.019	nd	nd
10	Mobara-7	92.4	97	1.1	0.049	0.046	0.022	0.004	nd
11	Yaizu-1	92.9	150	0.64	1.9	3.4	5.4	0.042	0.004
12	Yaizu-2	93.0	250	1.4	9.5	16	7.0	0.26	0.031
13	Yaizu-3	93.1	270	0.83	0.32	0.41	6.5	0.004	0.007
14	Shimizu	92.5	14	nd	nd	0.011	0.03	nd	nd
15	Fujieda-1	86.9	45	0.19	0.029	0.008	0.03	0.005	nd
16	Fujieda-2	87.9	40	0.11	0.018	nd	0.035	0.003	nd
17	Haibara	92.0	250	0.35	0.084	0.029	1.8	0.003	0.005
18	Sadohara-1	92.3	250	120	23	35	0.12	10	4.5
19	Sadohara-2	85.8	880	89	21	5.1	0.46	5.6	1.2
20	Sadohara-3	95.0	420	4.7	0.86	0.17	1.7	0.087	0.012
21	Shikine-1	49.3	63	2.3	0.22	0.23	0.068	0.060	0.031
22	Shikine-2	69.1	21	3.4	0.32	0.26	0.01	0.066	nd

[1] No.1 and No.2 are the same samples, and No.2 was measured 2 years after the measurement of No.1.
nd: not detected
* revised values

2.3 Discussion

The relation between the ratio of C_2H_6/C_3H_8 and that of neo-C_5H_{12}/iso-C_5H_{12} is shown in Fig. 7. The relation between the ratio of C_2H_6/C_3H_8 and that of neo-C_5H_{12}/iso-C_4H_{10} is shown in Fig. 8. The relation between the ratio of neo-C_5H_{12}/iso-C_5H_{12} and that of neo-C_5H_{12}/iso-C_4H_{10} is shown in Fig. 9. A log-log straight line correlation is observed between the ratios. There are three possible explanations for the log-log straight line correlations, that is, 1) compositional change due to the bacterial degradation process, 2) compositional change due to the dissolution in water and 3) compositional change due to the decomposition of hydrocarbons by hydrogen abstraction.

1) Bacterial degradation
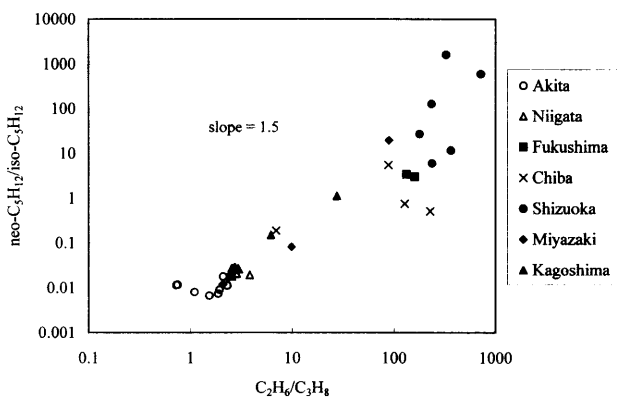
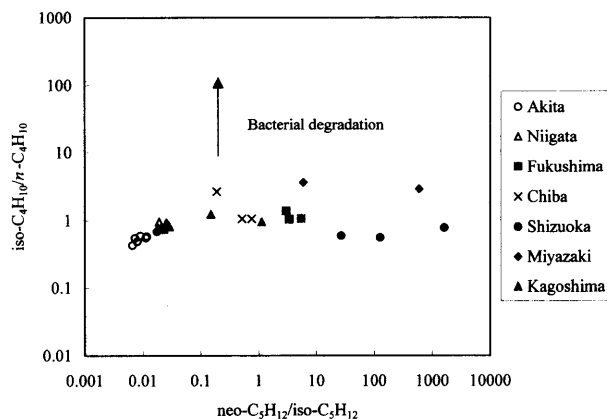Fig. 7   Cross-plot of C_2H_6/C_3H_8 and neo-C_5H_{12}/iso-C_5H_{12}.

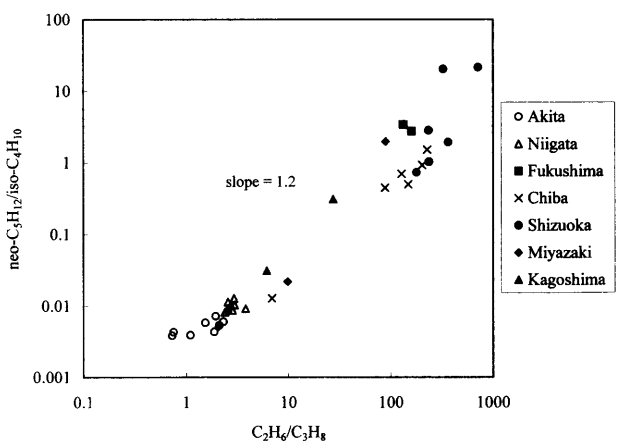Fig. 8   Cross-plot of C_2H_6/C_3H_8 and neo-C_5H_{12}/iso-C_4H_{10}.

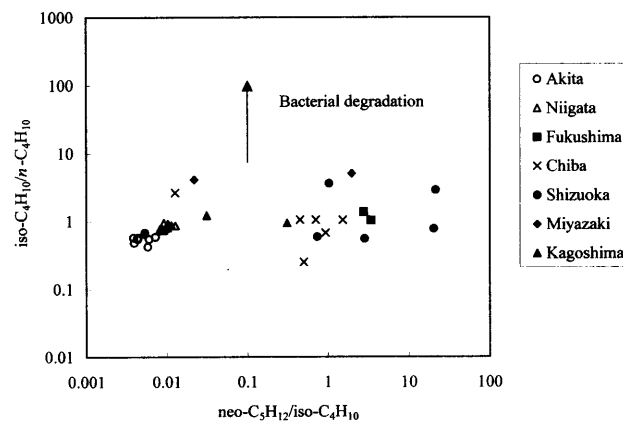Fig. 9   Cross-plot of neo-C_5H_{12}/iso-C_5H_{12} and neo-C_5H_{12}/iso-C_4H_{10}.
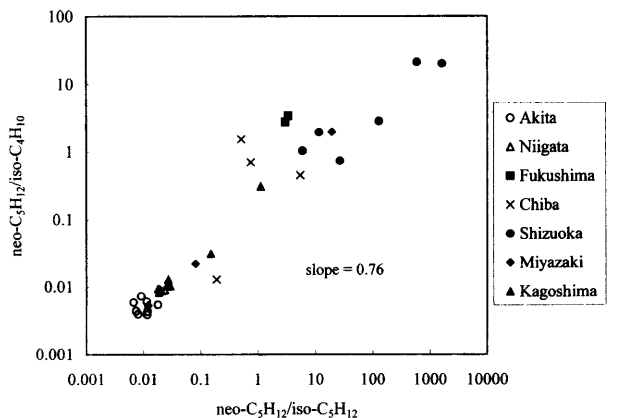

Fig. 10   Cross-plot of neo-C_5H_{12}/iso-C_5H_{12} and iso-C_4H_{10}/n-C_4H_{10}.

Fig. 11   Cross-plot of neo-C_5H_{12}/iso-C_4H_{10} and iso-C_4H_{10}/n-C_4H_{10}.
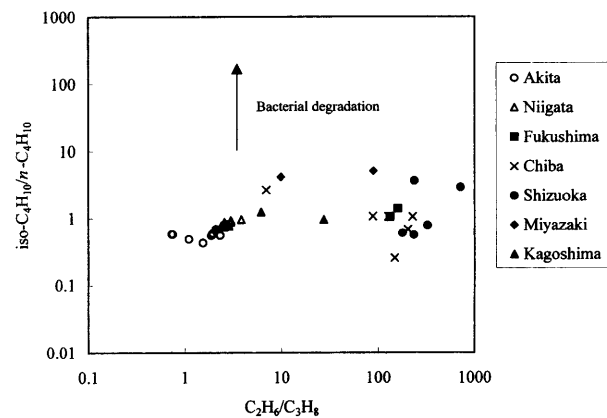

Fig. 12   Cross-plot of C_2H_6/C_3H_8 and iso-C_4H_{10}/n-C_4H_{10}.

It is known that the hydrocarbon composition of natural gas is changed by bacterial degradation (James, and Burns, 1984). In this case, n-alkanes are selectively degraded and the iso-C_4H_{10}/n-C_4H_{10} ratio increases with progression of bacterial degradation. The C_2H_6/C_3H_8 ratio also increases with progression of bacterial degrdation. However, the C_2H_6/C_3H_8 ratio also changes with decomposition by H abstraction as mentioned below. So, the iso-C_4H_{10}/n-C_4H_{10} ratio is used as a parameter of bacterial degradation. If the bacterial oxidation affects the neo-C_5H_{12}/iso-C_5H_{12}, neo-C_5H_{12}/iso-C_4H_{10} and C_2H_6/C_3H_8 ratios, it is expected that the ratios show straight line correlation with the iso-C_4H_{10}/n-C_4H_{10} ratio. The relation between neo-C_5H_{12}/iso-C_5H_{12} and iso-C_4H_{10}/n-C_4H_{10}, neo-C_5H_{12}/iso-C_4H_{10} and iso-C_4H_{10} /n-C_4H_{10}, and C_2H_6/C_3H_8 and iso-C_4H_{10}/n-C_4H_{10} are shown in Figs. 10, 11 and 12, respectively. The neo-C_5H_{12}/iso-C_5H_{12}, neo-C_5H_{12}/iso-C_4H_{10} and C_2H_6/C_3H_8 ratios do not show straight line correlations with the iso-C_4H_{10}/n-C_4H_{10} ratio. Therefore, it is concluded that bacterial degradation is not a major factor affecting the log-log straight line correlations in Figs. 7, 8 and 9.

2) Dissolution in water

The solubility in water of each hydrocarbon is shown in Table 5. There are two possible explanations concerned with the compositional change of natural gases; concentration of hydrocarbons in water and dilution of hydrocarbons due to extraction by water.

If a concentration of hydrocarbon in water occurs, it is expected that the C_2H_6/C_3H_8 ratio in natural gases becomes higher because the solubility of C_2H_6 in water is higher than that of C_3H_8. The neo-C_5H_{12}/iso-C_5H_{12} and neo-C_5H_{12}/iso-C_4H_{10} ratios decrease because the solubility of neo-C_5H_{12} in water is lower than those of

iso-C_4H_{10} and iso-C_5H_{12}. Therefore, it is expected that the neo-C_5H_{12}/iso-C_4H_{10} ratio increases with the increase of ratio neo-C_5H_{12}/iso-C_5H_{12}. This agrees with Fig. 15. With the increase of ratio C_2H_6/C_3H_8, the ratios neo-C_5H_{12}/iso-C_5H_{12} and neo-C_5H_{12}/iso-C_4H_{10} decrease. This does not agree with Figs. 13 and 14. Therefore, the concentration of
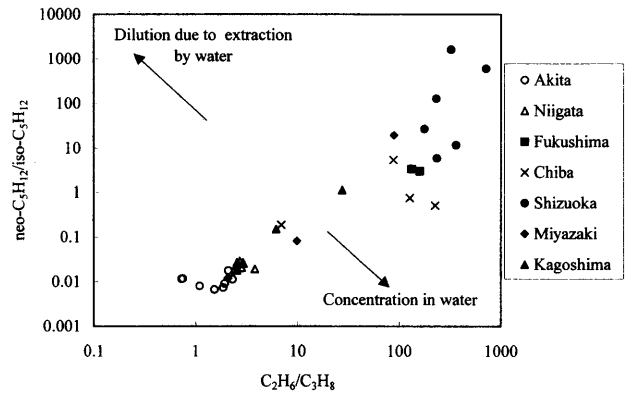
Fig. 13   Cross-plot of C_2H_6/C_3H_8 and neo-C_5H_{12}/iso-C_5H_{12} (Dissolution in water).
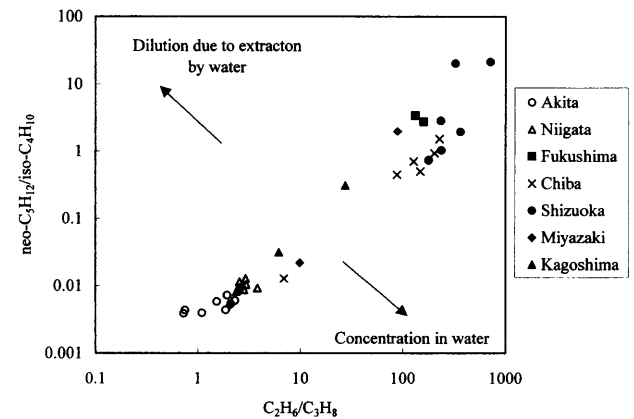
Fig. 14   Cross-plot of C_2H_6/C_3H_8 and neo-C_5H_{12}/iso-C_4H_{10} (Dissolution in water).
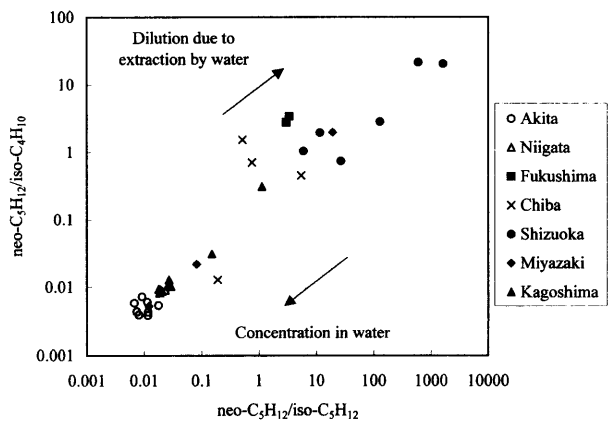
Table 5   Solubility of hydrocarbons in water.

	solubility in water mol/mol
CH_4	0.253×10^{-4}
C_2H_6	0.340×10^{-4}
C_3H_8	0.273×10^{-4}
iso-C_4H_{10}	0.146×10^{-4}
n-C_4H_{10}	0.224×10^{-4}
neo-C_5H_{12}	0.083×10^{-4}
iso-C_5H_{12}	0.121×10^{-4}
n-C_5H_{12}	0.110×10^{-4}

Data from the Chemical Society of Japan (1993) and IUPAC (1989)

Fig. 15   Cross-plot of neo-C_5H_{12}/iso-C_5H_{12} and neo-C_5H_{12}/iso-C_4H_{10} (Dissolution in water).

hydrocarbons in water is not considered as a major factor affecting the log-log straight line correlations in Figs. 7, 8 and 9.

If the dilution of hydrocarbons due to extraction by water occurs, the C_2H_6/C_3H_8 ratio in natural gases becomes lower because the solubility of C_2H_6 in water is higher than that of C_3H_8. The ratios neo-C_5H_{12}/iso-C_5H_{12} and neo-C_5H_{12}/iso-C_4H_{10} increase because the solubility of neo-C_5H_{12} in water is lower than those of iso-C_4H_{10} and iso-C_5H_{12}. Therefore, it is expected that ratio neo-C_5H_{12}/iso-C_4H_{10} decreases with the decrease of ratio neo-C_5H_{12}/iso-C_5H_{12}. This agrees with Fig. 15. With the decrease of ratio C_2H_6/C_3H_8, the ratios neo-C_5H_{12}/iso-C_5H_{12} and neo-C_5H_{12}/iso-C_4H_{10} increase. This does not agree with Figs. 13 and 14. Therefore, the dilution of hydrocarbons due to extraction by water is not considered as a major factor affecting the log-log straight line correlations in Figs. 7, 8 and 9.

Thus, the compositional change of natural gases due to dissolution in water is not considered as a major factor affecting the log-log straight line correlations in Figs. 7, 8 and 9.

3) Decomposition of hydrocarbons by hydrogen abstraction

The C-H bond dissociation energy is shown in Table 6. If some molecule or radical abstract hydrogen atom from hydrocarbons and decomposition of the hydrocarbon occurs, the hydrocarbon that has a low bond dissociation energy is selectively decomposed. The C-H bond dissociation energy of isopentane is not known. However, it is expected that the energy is similar to that of isobutane, because both isopentane and isobutane have a tertiary carbon atom that links to a hydrogen atom. By the decomposition of hydrocarbons, it is expected that the ratios neo-C_5H_{12}/iso-C_5H_{12}, C_2H_6/C_3H_8 and neo-C_5H_{12}/iso-C_4H_{10} increase. These trends are well demonstrated in Figs. 16, 17 and 18.

A radical that is expected to abstract hydrogen from a hydrocarbon is the hydroxyl radical. A very little portion of underground water is inferred to be decomposed to H and OH radicals naturally. The decomposition reaction of hydrocarbons by the hydroxyl radical

in the gas phase is a second order reaction. However, under the condition where the hydroxyl radical concentration is constant, the reaction becomes a first order reaction (Parrish *et al*, 1992). The concentration of each hydrocarbon is given by Eqs. (1), (2), (3) and
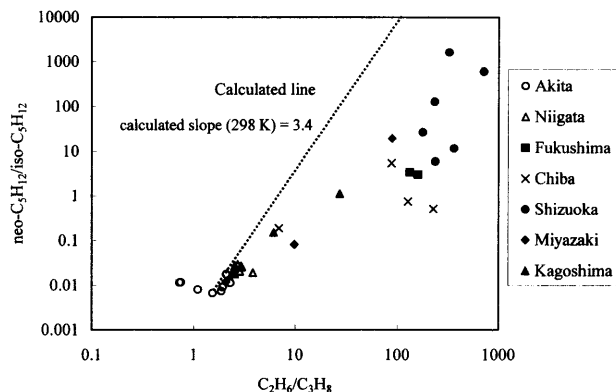
Fig. 16 Cross-plot of C_2H_6/C_3H_8 and neo-C_5H_{12}/iso-C_5H_{12} (Decompositiopn by H abstraction).
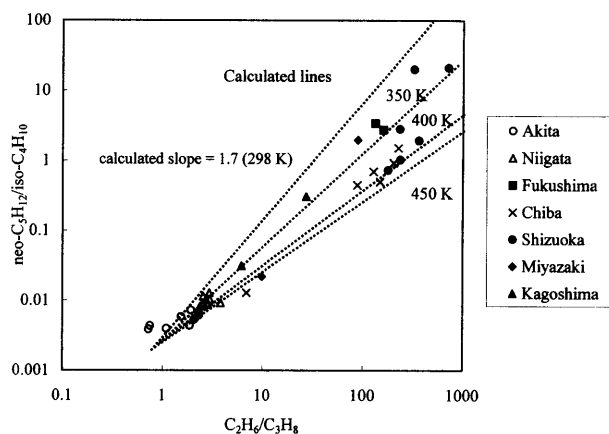
Fig. 17 Cross-plot of C_2H_6/C_3H_8 and neo-C_5H_{12}/iso-C_4H_{10} (Decomposition by H abstraction).

Table 6 Bond dissociation energy.

	kJ/mol
C_2H_5-H	410
iso-C_3H_7-H	395
tert-C_4H_9-H	386
neo-C_5H_{11}-H	415

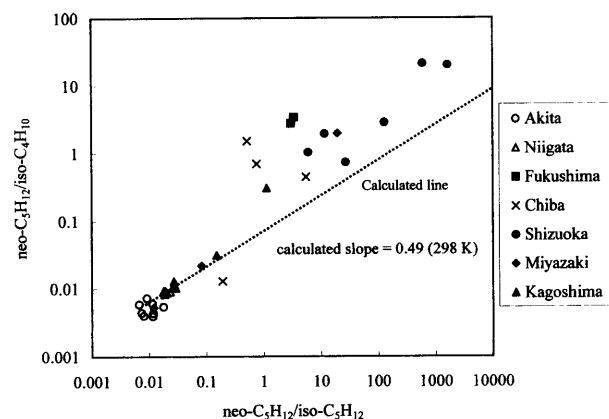Calculated by data from the Chemical Society of Japan (1984)

Fig. 18 Cross-plot of neo-C_5H_{12}/iso-C_5H_{12} and neo-C_5H_{12}/iso-C_4H_{10} (Decomposion by H abstraction).

(4). In Eqs. (1), (2), (3) and (4), [A] , [B] , [C] and [D] are the concentrations of hydrocarbons A, B, C and D, respectively. The initial concentrations of $[A]_0$, $[B]_0$, $[C]_0$ and $[D]_0$ are for hydrocarbons A, B, C and D, respectively. The decomposition rate constants k_A, k_B, k_C and k_D are for hydrocarbons A, B, C and D, respectively. [OH] is the concentration of the hydroxyl radical and t is the reaction time.

$$[A] = [A]_0 \exp(-k_A[OH]t) \quad (1)$$

$$[B] = [B]_0 \exp(-k_B[OH]t) \quad (2)$$

$$[C] = [C]_0 \exp(-k_C[OH]t) \quad (3)$$

$$[D] = [D]_0 \exp(-k_D[OH]t) \quad (4)$$

After rearrangement of Eqs. (1), (2), (3) and (4),

$$\ln[A] = \ln[A]_0 - k_A[OH]t \quad (5)$$

$$\ln[B] = \ln[B]_0 - k_B[OH]t \quad (6)$$

$$\ln[C] = \ln[C]_0 - k_C[OH]t \quad (7)$$

$$\ln[D] = \ln[D]_0 - k_D[OH]t \quad (8)$$

From Eqs. (5) and (6),

$$\ln[A]/[B] - \ln[A]_0/[B]_0 = -(k_A - k_B)[OH]t \quad (9)$$

From Eqs. (7) and (8),

$$\ln[C]/[D] - \ln[C]_0/[D]_0 = -(k_C - k_D)[OH]t \quad (10)$$

From Eqs. (9) and (10)

$$\log([A]/[B]) = M \log([C]/[D]) + N, \quad (11)$$

where

$$M = (k_A - k_B)/(k_C - k_D) \quad (12)$$

$$N = \log([A]_0/[B]_0) - M \log([C]_0/[D]_0) \quad (13)$$

Equation (11) means there is a straight line relation between the $\log([A]/[B])$ and $\log([C]/[D])$. The slope M can be calculated from Eq. (12). The relative rate constants of the hydrocarbon decomposition reactions by hydroxyl radicals in gas phases are shown in Table 7 (Atkinson, 1990). Calculated lines are shown in Figs. 16, 17 and 18. These lines show the similar tendency with measured results (positive slopes). If the decomposition occurs in the liquid phase, or other radicals or molecules abstract H atoms, it is expected that a same tendency is obtained, because the hydrocarbon decomposition rate is governed by the hydrocarbon

Table 7 Relative rate constants for the reaction of OH radicals with alkanes.

Alkane	Relative rate constants			
	298K	350K	400K	450K
CH_4	1	3	5	10
C_2H_6	32	56	86	123
C_3H_8	138	194	257	330
iso-C_4H_{10}	280	336	398	453
n-C_4H_{10}	304	381	465	558
neo-C_5H_{12}	102	154	215	286
iso-C_5H_{12}	467	ND	ND	ND
n-C_5H_{12}	471	581	702	835

Calculated from data by Atkinson (1990)
ND: no data

structure. Therefore, it is inferred that decomposition by H abstraction is the major factor of the hydrocarbon composition of natural gases.

It is known that the hydroxyl radical is generated by UV light irradiation of water (Parrish *et al.*, 1992). In Figs. 7, 8 and 9, the two data points for Fukushima are of the same sample. One was analyzed 6 days after the sampling, and the other was analyzed 2 years after the sampling. The difference between the two data in Figs. 7, 8 and 9 is not observed. Therefore, degradation of the samples under the preservation condition can be ignored.

3. Fractionation of light hydrocarbons through gas chromatographic (GC) columns packed with rocks and minerals - Implications for natural gas migration

3.1 Experiments
Samples

Samples used in the simulation experiments are listed in Table 8. Samples were pulverized and mixed with quartz sand. The content of montmorillonite in Sample No. 11 is about 50 %. Sample Nos. 12-18 are composed of almost pure clay minerals or zeolites. The types of clay minerals or zeolites were determined by a X-ray diffractometer (CuKa, 40 kV, 150 mA).

Simulation experiments

Stainless steel columns (1 m x 2 mm I. D.) were packed with powdered rock and mineral samples and installed into a GC (HP 5890A) with an FID detector. The columns were preheated for 0 to 20 h at 90 ℃, passing helium gas. The column temperature was then maintained at 50 ℃. One ml of each hydrocarbon was injected and its retention time was measured using helium as a carrier gas. Hydrocarbons examined were methane, ethane, propane, isobutane, n-butane, isopentane and n-pentane (Fig. 19).

Table 8   Samples used for GC column packing.

No.	Location	Contained clay minerals or zeolites
1 Mudstone (30-80 mesh)	Niigata (Nishiyana Formation)	Montmorillonite
2 Sandstone (30-80 mesh)	Akita (Onnagawa Formation)	Montmorillonite
3 Limestone (30-80 mesh)	Hokkaido (JLs-1*)	nd
4 Dolomite (30-80 mesh)	Tochigi (Jdo-1*)	nd
5 Tuff (30-80 mesh)	Akita (Lower Nanatani tuff)	Montmorillonite
6 Basalt (30-80 mesh)	Nagasaki (JB-1*)	Montmorillonite
7 Granite (30-80 mesh)	Gifu (JG-2*)	nd
8 Rhyolite (30-80 mesh)	Nagano (JR-1*)	nd
9 Andesite (30-80 mesh)	Kanagawa (JA-1*)	Montmorillonite
10 Andesite (30-80 mesh)	Gunma (JA-3*)	nd
11 Montmorillonite (80 mesh under)/Quartz sand (1/20)	Yamagata (Tsukinuno mine)	Montmorillonite
12 Talc (80 mesh under)/Quartz sand (1/20)	North Korea (Wako Pure Chemical Co. Ltd.)	Talc
13 Halloysite (80 mesh under)/Quartz sand (1/20)	Nagano (ina kaolin)	Halloysite
14 Sericite (80 mesh under)/Quartz sand (1/30)	Shimane (Nabeyama mine)	Sericite
15 Chlorite (80 mesh under)/Quartz sand (1/20)	Ibaraki (Hase mine)	Chlorite
16 Vermiculite (80 mesh under)/Quartz sand (1/20)	South Africa (Palabora mine)	Vermiculite
17 Clinoptilolite (30-80 mesh)/Quartz sand (1/8)	Akita (Futatsui mine)	Clinoptilolite
18 Mordenite (30-80 mesh)/Quartz sand (1/150)	Miyagi (Shiroishi mine)	Mordenite
19 Kerogen (80 mesh under)/Quartz sand (1/50)	Wakayama Tanabe Group	
20 Coal (80 mesh under)/Quartz sand (1/10)	Hokkaido (Minamiooyuubari mine)	
21 Coal (80 mesh under)/Quartz sand (1/10)	Hokkaido (Kushiro mine)	
22 Molecular sieves 3A (30-80 mesh)	(Wako Pure Chemical Co. Ltd.)	
23 Molecular sieves 5A (30-80 mesh)/Quartz sand (1/70)	(Wako Pure Chemical Co. Ltd.)	
24 Molecular sieves 5A (No. 23)/Molecular sieves 3A (No. 22)/Quartz sand (1/2/50)	(Wako Pure Chemical Co. Ltd.)	
25 Quartz sand (30-80 mesh)	China (Wako Pure Chemical Co. Ltd.)	nd

nd: not detected
*: Rock reference samples of the Geological Survey of Japan

CH_4, C_2H_6, C_3H_8, iso-C_4H_{10}, n-C_4H_{10}, iso-C_5H_{12}, n-C_5H_{12}
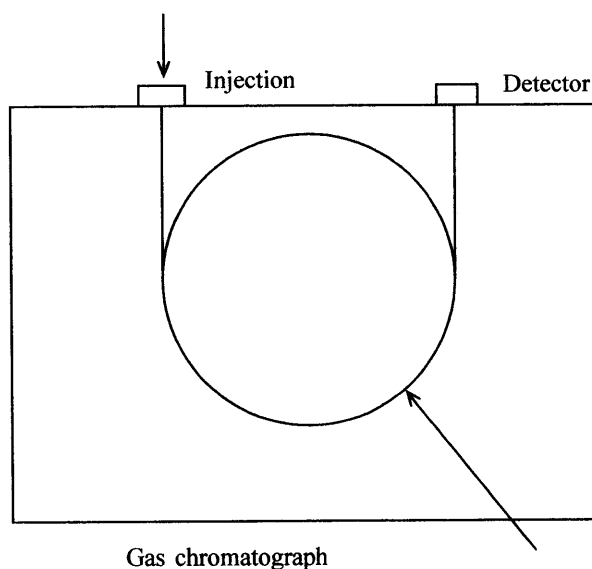
Fig. 19   Simulation experiment.

3.2 Results

The retention time of each hydrocarbon when the rock and mineral samples were aged for a fixed period (18 or 20 hours) is shown in Table 9. Under the conditions used in this examination, the retention time of methane was the smallest among the seven hydrocarbons, ranging from 0.09 min (Nos. 18 and 25) to 0.24 min (No. 22), depending on the materials packed in the GC column. When Nos. 1, 2, 5, 6, 9, 11, 12, 13, 14, 15, 16, 18, 19 and 22 were used, the retention

Table 9 Retention times of hydrocarbons on GC columns packed with various rock and mineral samples with fixed aging period (18 or 20 hours) (Igari and Sakata, 1992).

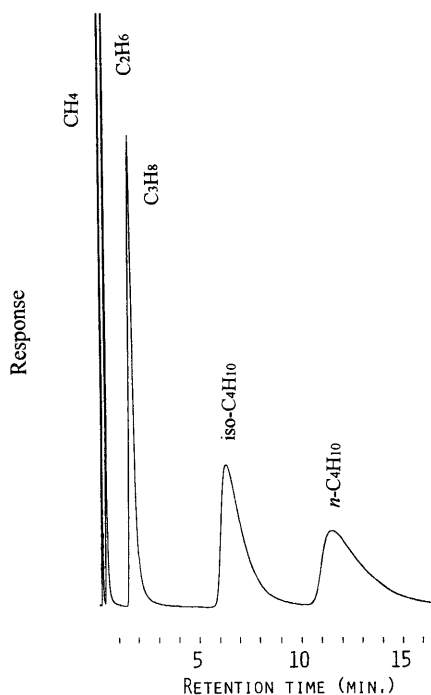| No.	Flow rate of carrier gas (ml/min.)	Aging time /h	Retention time /min						
			CH_4	C_2H_6	C_3H_8	iso-C_4H_{10}	n-C_4H_{10}	iso-C_5H_{12}	n-C_5H_{12}
1	29.3	20	0.17	0.37	1.61	6.50	11.59		
2	28.4	20	0.22	0.37	1.14	3.12	7.20		
3	29.0	18	0.13	0.13	0.13	0.14	0.14	0.14	0.14
4	29.1	20	0.11	0.11	0.11	0.12	0.12	0.12	0.12
5	29.0	20	0.17	0.25	0.66	1.88	3.63		
6	28.8	20	0.10	0.13	0.23	0.50	1.13	3.01	9.00
7	29.1	18	0.10	0.09	0.10	0.09	0.10	0.09	0.10
8	29.1	18	0.10	0.09	0.09	0.09	0.10	0.09	0.09
9	28.7	20	0.12	0.14	0.28	0.72	1.30	4.17	9.01
10	28.8	18	0.10	0.10	0.10	0.10	0.10	0.10	0.11
11	28.4	18	0.13	0.13	0.15	0.19	0.23	0.48	0.74
12	21.4	20	0.19	0.19	0.19	0.20	0.20	0.22	0.22
13	28.6	20	0.11	0.14	0.25	0.65	1.00	3.70	6.65
14	22.1	18	0.21	0.21	0.21	0.23	0.23	0.29	0.32
15	23.6	18	0.19	0.19	0.19	0.20	0.20	0.23	0.24
16	27.9	20	0.14	0.16	0.21	0.29	0.56	1.00	3.17
17	29.1	20	0.10	0.29	1.02	0.22	6.70	0.70	
18	28.7	20	0.09	0.14	0.27	0.40	3.00		
19	28.7	18	0.12	0.12	0.13	0.13	0.15	0.15	0.22
20	26.1	20	0.17	0.17	0.17	0.17	0.17	0.18	0.19
21	28.2	18	0.14	0.14	0.14	0.14	0.14	0.15	0.15
22	28.4	20	0.15	0.16	0.20	0.30	0.32	0.63	0.72
23	29.0	20	0.11	0.25	1.58	0.09	21.47	0.09	
24	29.4	20	0.13	0.25	1.12	0.21	17.78	0.40	
25	29.4	20	0.09	0.09	0.09	0.09	0.09	0.08	0.08

Fig. 20 Gas chromatogram of light hydrocarbons using a column packed with mudstone (No. 1) and aged for 20 hours.

time changed divergently with increasing molecular size from methane to pentane. In these cases, isoalkanes eluted relatively faster than n-alkanes when compared with the same carbon numbered molecules. When Nos. 17 and 24 were used, the order of retention time was $CH_4 <$ iso-$C_4H_{10} < C_2H_6 <$ iso-$C_5H_{12} < C_3H_8 < n$-C_4H_{10}. When No. 23 was used, the order was iso-$C_4H_{10} =$ iso-$C_5H_{12} < CH_4 < C_2H_6 < C_3H_8 < n$-$C_4H_{10}$. When Nos. 3, 4, 7, 8, 10, 20, 21 and 25 were used, retention times of the hydrocarbons were almost the same in each sample.

Retention times of the hydrocarbons when the mineral samples were aged for various periods (0 to 20 h) are shown in Table 10. When Nos. 11, 13, 16, 17 and 18 were used, the retention time of each hydrocarbon increased with an increase of aging time except for CH_4 in Nos. 11, 13, 16, 17 and 18, and C_2H_6 in Nos. 11 and 16. When Nos. 12, 14 and 15 were used, retention times of each hydrocarbon did not change. When No. 1 was used for column packing, aged for 20 h, and injected together with CH_4, C_2H_6, C_3H_8, iso-C_4H_{10} and n-C_4H_{10}, its chromatogram is shown in Fig. 20.

Table 10　Retention times of hydrocarbons on GC columns packed with various mineral samples with various aging periods (0-20 h) (Igari and Sakata, 1992).

Clay minetral or zeolite	Aging time /h	Retention time /min.						
		CH_4	C_2H_6	C_3H_8	iso-C_4H_{10}	n-C_4H_{10}	iso-C_5H_{12}	n-C_5H_{12}
No. 11	0.0	0.13	0.13	0.13	0.14	0.15	0.20	0.29
Montmorillonite	0.5	0.13	0.13	0.15	0.20	0.24	0.52	0.78
(Clay mineral)	2.0	0.13	0.13	0.15	0.20	0.24	0.51	0.77
	4.0	0.13	0.13	0.15	0.20	0.24	0.51	0.77
	18.0	0.13	0.13	0.15	0.19	0.23	0.48	0.74
No. 12	0.0	0.19	0.19	0.19	0.20	0.20	0.22	0.22
Talc	0.5	0.19	0.19	0.19	0.20	0.20	0.22	0.22
(Clay mineral)	2.0	0.19	0.19	0.19	0.20	0.20	0.22	0.22
	4.0	0.19	0.19	0.19	0.20	0.20	0.22	0.22
	20.0	0.19	0.19	0.19	0.20	0.20	0.22	0.22
No. 13	0.0	0.11	0.11	0.12	0.15	0.17	0.35	0.58
Halloysite	0.5	0.11	0.13	0.24	0.65	0.98	3.76	6.79
(Clay mineral)	2.0	0.11	0.14	0.25	0.67	1.04	3.90	7.28
	4.0	0.11	0.14	0.25	0.68	1.05	3.94	7.32
	20.0	0.11	0.14	0.25	0.65	1.00	3.70	6.65
No. 14	0.0	0.21	0.21	0.21	0.23	0.24	0.31	0.35
Sericite	0.5	0.20	0.21	0.21	0.23	0.24	0.31	0.35
(Clay mineral)	2.0	0.20	0.21	0.21	0.23	0.24	0.30	0.34
	4.0	0.21	0.21	0.21	0.23	0.24	0.30	0.33
	18.0	0.21	0.21	0.21	0.23	0.23	0.29	0.32
No. 15	0.0	0.19	0.19	0.19	0.20	0.20	0.23	0.23
Chlorite	0.5	0.19	0.19	0.19	0.20	0.20	0.23	0.24
(Clay mineral)	2.0	0.19	0.19	0.19	0.20	0.20	0.23	0.24
	4.0	0.19	0.19	0.19	0.20	0.20	0.23	0.24
	18.0	0.19	0.19	0.19	0.20	0.20	0.23	0.24
No. 16	0.0	0.16	0.16	0.17	0.18	0.18	0.22	0.24
Vermiculite	0.5	0.14	0.15	0.19	0.25	0.41	0.73	1.93
(Clay mineral)	2.0	0.14	0.15	0.21	0.29	0.60	1.05	3.28
	4.0	0.14	0.16	0.21	0.29	0.60	1.05	3.46
	20.0	0.14	0.16	0.21	0.29	0.56	1.00	3.17
No. 17	0.0	0.09	0.09	0.10	0.11	0.12	0.16	0.28
Clinoptilolite	0.5	0.09	0.13	0.30	0.19	1.76	0.55	
(Zeolite)	2.0	0.10	0.17	0.55	0.21	3.53	0.64	
	4.0	0.10	0.20	0.70	0.22	4.54	0.66	
	20.0	0.10	0.29	1.02	0.22	6.70	0.70	
No. 18	0.0	0.09	0.09	0.09	0.09	0.09		
Mordenite	0.5	0.09	0.10	0.11	0.11	0.27		
(Zeolite)	2.0	0.09	0.11	0.18	0.11	1.31		
	4.0	0.09	0.12	0.23	0.15	2.17		
	20.0	0.09	0.14	0.27	0.40	3.00		

3.3　Discussion

The migration of natural gases from source rocks to reservoirs can be divided into two stages. One is the primary stage in which natural gases start migration from the source rocks, normally mudstone in Japan. The other is the secondary stage in which gases migrate into reservoir rocks such as sandstone, limestone and dolomite. Tuffs and other volcanic rocks are also

important reservoir rocks in Japan. In the measurement of retention time for the hydrocarbons (Table 9), main constituents of the source rocks and re-servoir rocks (Nos. 1-10) were used as column packing and aged for fixed period (18 or 20 hours). A difference of retention time was observed only when the rock samples contained clay minerals (Table 8). This result indicates that the existence of clay minerals is an important factor for fractionation during migration.

Another possible factor affecting fractionation is the existence of kerogen. The kerogen content in mud-stone in Japan is usually less than 2 %. Retention times of the light hydrocarbons when kerogen or coal (Nos. 19-21) diluted with quartz sand was used as column packing and aged for a fixed period (18 or 20 hours) are shown in Table 9. Fractionation was observed when kerogen was used, but it was very small. Thus, the existence of kerogen is not considered to be a major factor for fractionation among the hydrocarbons during migration.

During the primary migration of gases, one of the main clay minerals present in the migration route is illite because expandable clay minerals such as mont-morillonite are converted to illite in the generation stage of gaseous hydrocarbons (Powers, 1967; Burst, 1969; Perry and Hower, 1970; 1972). During the secondary migration, many kinds of clay minerals may be present in the migration routes. Figure 21 shows the relative retention volumes (C_nH_m/CH_4) of light hydrocarbons when several kinds of clay minerals were used as column packing and aged for fixed period (18 or 20 hours). Sericite (No. 14) was used in place of illite in this experiment because their structures are similar. Large fractionation occurred when the expandable clay minerals such as montmorillonite (No. 11), halloysite (No. 13) and vermiculite (No. 16) were used. Little fractionation occurred when the unexpandable talc (No. 12), sericite (No. 14) and chlorite (No. 15) were used. These results show that clay minerals cause
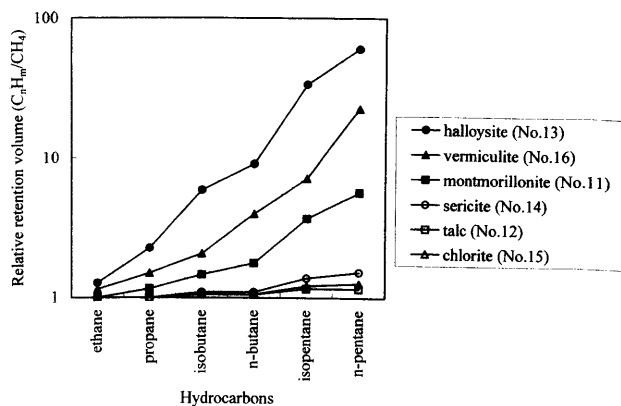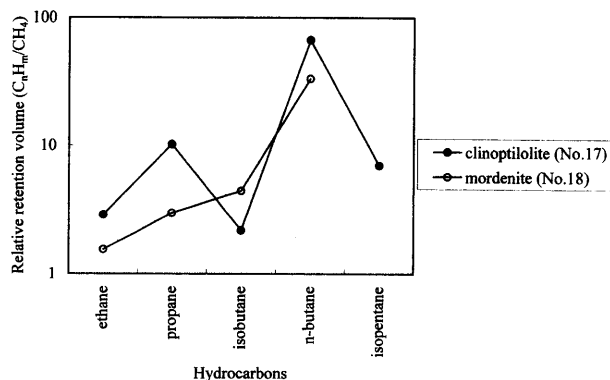

Fig. 22 Relative retention volumes (C_nH_m/CH_4) of light hydrocarbons using columns packed with zeolites.

large fractionation when they have expandable inter-layer spaces.

Figure 22 shows the relative retention volumes of light hydrocarbons when zeolites (clinoptilolite (No. 17) and mordenite (No. 18)) were used as column packing and aged for 20 hours. These zeolites are commonly found in Japanese tuffaceous rocks (Hujioka and Yoshikawa, 1969; Hujioka and Sakai, 1971; Kano, 1977; Negishi, 1981), which are the main reservoir rocks in Japan. These zeolites may be present in secondary migration routes.

For mordenite, the order of retention time is normal: $CH_4 < C_2H_6 < C_3H_8 < iso\text{-}C_4H_{10} < n\text{-}C_4H_{10}$. Torii *et al.* (1977) conducted a similar experiment using clinoptilo-lite which is known to have two kinds of pores. They reported that the order was $CH_4 < iso\text{-}C_4H_{10}$ and that other hydrocarbons did not elute. By diluting clinop-tilolite with quartz sand, the order was following: $CH_4 < iso\text{-}C_4H_{10} < C_2H_6 < iso\text{-}C_5H_{12} < C_3H_8 < n\text{-}C_4H_{10}$. Isoalkanes eluted relatively faster than n-alkanes. When molecular sieves 5A (No. 23) was used, isoal-kanes also eluted relatively faster: $iso\text{-}C_4H_{10} = iso\text{-}C_5H_{12} < CH_4 < C_2H_6 < C_3H_8 < n\text{-}C_4H_{10}$. This is be-cause n-alkanes are selectively adsorbed by the pores whose size (5 Å) is between the cross-sectional di-ameters of isoalkanes and n-alkanes (Table 11). When

Fig. 21 Relative retention volumes (C_nH_m/CH_4) of light hydrocarbons using columns packed with clay minerals.

Table 11 Cross-sectional diameters of molecules (Angstrom)

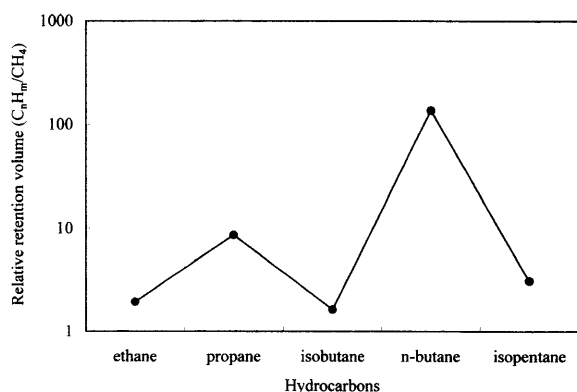|	
CH_4	4.00
C_2H_6	4.00
C_3H_8	4.89
$iso\text{-}C_4H_{10}$	5.58
$n\text{-}C_4H_{10}$	4.89
$iso\text{-}C_5H_{12}$	5.58
$n\text{-}C_5H_{12}$	4.89

Barrer and Ibbitson (1944)

Fig. 23 Relative retention volumes (C_nH_m/CH_4) of light hydrocarbons using columns packed with MS5A/MS3A/Qz sand (1/2/50).

using molecular sieves 3A whose pore size is 3 Å (No. 22), the order was $CH_4 < C_2H_6 < C_3H_8 < iso\text{-}C_4H_{10} < n\text{-}C_4H_{10} < iso\text{-}C_5H_{12} < n\text{-}C_5H_{12}$. When using mixture of molecular sieves 3A, 5A and quartz sand (No. 24), the order was $CH_4 < iso\text{-}C_4H_{10} < C_2H_6 < iso\text{-}C_5H_{12} < C_3H_8 < n\text{-}C_4H_{10}$ (Fig. 23). This result is similar to the one when clinoptilolite was used. From these facts, it is concluded that one pore of clinoptilolite adsorbs n-alkanes selectively because its cross-sectional diameters is smaller than 5 Å, while the other pore causes normal fractionation because the diameters of all the alkanes are larger than 3 Å.

The relative retention volumes $(n\text{-}C_5H_{12}/CH_4)$ using clay minerals and zeolites that were aged for various periods (0 to 20 h) are shown in Figs. 24 and 25 respectively. For expandable clay minerals and zeolites, the fractionation became larger with increase of aging time. When not aged, only small fractionation was observed. These results indicate that the dehydrated pores of zeolites cause fractionation. Furthermore, it is concluded by these results that fractionation by clay minerals or zeolites is insignificant under normal subsurface conditions where these minerals are hydrated.
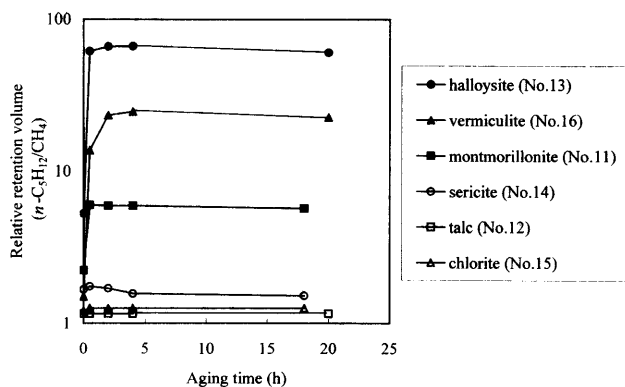

Fig. 24 Relative retention volumes $(n\text{-}C_5H_{12}/CH_4)$ with various aging periods using columns packed with clay minerals.
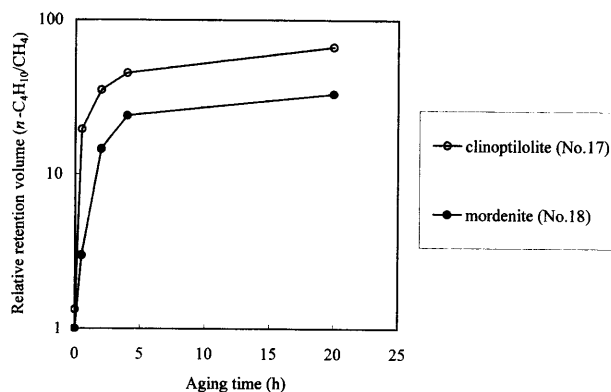

Fig. 25 Relative retention volumes $(n\text{-}C_4H_{10}/CH_4)$ with various aging periods using columns packed with zeolites.

4. Carbon isotopic ratios of methane, ethane and propane in natural gases in Japan: Origins of the gases and factors affecting the isotopic ratios

4.1 Carbon isotopic ratios of methane in dissolved-in-water type gases: Origins of dissolved-in-water type gases.

4.1.1 Experiments
Samples

Dissolved-in-water type gas samples were collected from several gas fields in Fukushima, Chiba, Shizuoka, Miyazaki and Kagoshima prefectures (Fig. 2-1, Table 1). The sampling procedures are the same as that for the chemical analysis.

Analysis

Methane in each sample was separated with a Shimadzu 4CPF gas chromatograph (TCD detector) and introduced into a CuO combustion tube kept at 850 ℃. The produced CO_2 and H_2O were collected at the tempeature of liquid nitrogen, and separated at the temperature of dry ice-ethanol mixture. The carbon isotopic ratio of CO_2 was measured with a Varian MAT 250 mass spectrometer (Fig. 26).

<div align="center">

Separation of each hydrocarbon by a gas chromatograph
(Packed column packed with silica gel)
↓
Oxidation to CO_2 by heating with CuO at 850℃
↓
Collection and purification of CO_2 by cryogenic distillation
↓
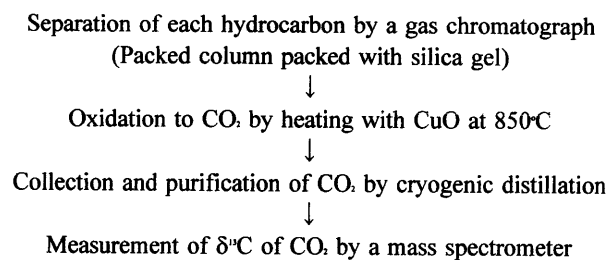Measurement of $\delta^{13}C$ of CO_2 by a mass spectrometer

</div>

Fig. 26 Analytical method of carbon isotopic ratios $(^{13}C/^{12}C)$.

4.1.2 Results

The carbon isotopic compositions of methane in the samples are listed in Table 12 (No. 1 for the gas field

Table 12 Dissolved-in-water type gases and their carbon isotopic ratios of methane.

No.	Area	Gas field	$\delta^{13}C(CH_4)$ /‰
1	*Fukushima*	Nakoso	-45.3
3	*Chiba*	Narashino*	-67.8
4	*Chiba*	Mobara-1*	-67.0
5	*Chiba*	Mobara-2*	-67.1
6	*Chiba*	Mobara-3*	-66.5
7	*Chiba*	Mobara-4*	-66.9
8	*Chiba*	Mobara-5*	-67.0
9	*Chiba*	Mobara-6*	-67.0
10	*Chiba*	Mobara-7*	-67.3
11	*Shizuoka*	Yaizu-1*	-33.8
12	*Shizuoka*	Yaizu-2*	-34.2
13	*Shizuoka*	Yaizu-3*	-34.3
14	*Shizuoka*	Shimizu	-46.8
15	*Shizuoka*	Fujieda-1	-43.4
16	*Shizuoka*	Fujieda-2	-43.5
17	*Shizuoka*	Haibara	-38.0
18	*Miyazaki*	Sadohara-1*	-67.2
19	*Miyazaki*	Sadohara-2	-59.8
20	*Miyazaki*	Sadohara-3*	-66.4
21	*Kagoshima*	Shikine-1	-24.2
22	*Kagoshima*	Shikine-2	-26.8

* Igari and Sakata (1989)

in Fukushima, Nos. 3 to 10 for those in Chiba, Nos. 11 to 17 for those in Shizuoka, Nos. 18 to 20 for those in Miyazaki, and Nos. 21 and 22 for those in Kagoshima).

For the samples from Fukushima, $\delta^{13}C(CH_4)$ value was -45.3 ‰. For the samples from Chiba, the range of $\delta^{13}C(CH_4)$ values were -67.8 ~ -66.5 ‰. For the samples from Shizuoka, the range, of $\delta^{13}(CH_4)$ values were - 46.8 ~ -33.8 ‰ . For the samples from Miyazaki, the range of $\delta^{13}C(CH_4)$ values were -67.2 ~ -59.8 ‰ . For the samples from Kagoshima, the range of $\delta^{13}C(CH_4)$ values were -26.8 ~ -24.2 ‰.

4.1.3 Discussion

Biogenic gases show low $\delta^{13}C(CH_4)$ values (about -60 ~ -80 ‰) and contain small amounts of non-methane hydrocarbons (Rice and Claypool, 1981). On the other hand, thermogenic gases show high $\delta^{13}C(CH_4)$ values (about -25 ~ -45 ‰) and contain larger amounts of saturated nonmethane hydrocarbons. The latter is often associated with crude oil. Thermogenic gases may lose nonmethane hydrocarbons during migration without significant changes in $\delta^{13}C(CH_4)$ values (Sackett *et al.*, 1966; Schoell, 1983).

The estimated origins of the samples are listed in Table 13. The dissolved-in-water type gas samples from the Narashino (No. 3), and Mobara (Nos. 4 to 10) gas fields in Chiba, and the Sadohara (Nos. 18 and 20) gas field in Miyazaki are clearly of biogenic origin, judging from their low $\delta^{13}C(CH_4)$ values (-67.8 ~ -66.4 ‰). Natural gases of this type correspond to

Table 13 Origins of dissolved-in-water type gases.

No.	Area	Gas field or gas sign	$\delta^{13}C(CH_4)$ /‰	Origin
1	*Fukushima*	Nakoso	-45.3	Mixed
3	*Chiba*	Narashino	-67.8	Biogenic
4	*Chiba*	Mobara-1	-67.0	Biogenic
5	*Chiba*	Mobara-2	-67.1	Biogenic
6	*Chiba*	Mobara-3	-66.5	Biogenic
7	*Chiba*	Mobara-4	-66.9	Biogenic
8	*Chiba*	Mobara-5	-67.0	Biogenic
9	*Chiba*	Mobara-6	-67.0	Biogenic
10	*Chiba*	Mobara-7	-67.3	Biogenic
11	*Shizuoka*	Yaizu-1	-33.8	Thermogenic
12	*Shizuoka*	Yaizu-2	-34.2	Thermogenic
13	*Shizuoka*	Yaizu-3	-34.3	Thermogenic
14	*Shizuoka*	Shimizu	-46.8	Mixed
15	*Shizuoka*	Fujieda-1	-43.4	Thermogenic
16	*Shizuoka*	Fujieda-2	-43.5	Thermogenic
17	*Shizuoka*	Haibara	-38.0	Thermogenic
18	*Miyazaki*	Sadohara-1	-67.2	Biogenic
19	*Miyazaki*	Sadohara-2	-59.8	Mixed
20	*Miyazaki*	Sadohara-3	-66.4	Biogenic
21	*Kagoshima*	Shikine-1	-24.2	Thermogenic
22	*Kagoshima*	Shikine-2	-26.8	Thermogenic

those which have widely been found in Japan (Nakai, 1960; Nakai *et al.*, 1972; Waseda and Omokawa, 1988).

On the other hand, the samples from the Nakoso gas field (No. 1) in Fukushima, Yaizu gas field (Nos. 14 to 16), Shimizu gas field (No. 14), Fujieda gas field (Nos. 15 and 16) and Haibara gas field (No. 17) in Shizuoka, and Shikine gas field in Kagoshima (Nos. 21 and 22) are interpreted as thermogenic gases because of their high $\delta^{13}C(CH_4)$ values (-46.8 ~ -24.2 ‰). The sample from the Sadohara gas field (No. 19) is interpreted as a mixture of biogenic and thermogenic gases because of the intermediate $\delta^{13}C(CH_4)$ value. The occurrence of dissolved-in-water type gas of biogenic origin with a small mixing of thermogenic gas was reported by Waseda and Omokawa (1988). They explained that this type of gas was formed by an injection of thermogenic gas that migrated from a relatively deep reservoir into a dissolved-in-water type gas of biogenic origin in a relatively shallow formation water. The occurrence of the dissolved-in-water type gas of thermogenic origin found in the present study could be explained in the same way; thermogenic gas formed in a relatively deep reservoir migrated into a relatively shallow formation water.

4.2 Carbon isotopic ratios of methane, ethane and propane in oil field gases: Factors affecting the isotopic ratios.

4.2.1 Experiments
Samples and Analysis

Natural gas samples were collected from several oil and gas fields in Niigata and Akita as shown in Fig. 2-2. All samples were collected from different wells. The outline of the area has been described by Sakata (1991). The sampling procedures are the same as that for chemical analysis.

Methane, ethane and propane in each sample were separated with a Shimadzu 4CPF gas chromatograph (TCD detector). The analytical procedures for carbon isotopes are the same as that for dissolved-in-water type gases.

4.2.2 Results

Table 14 shows the results. For the samples from Niigata, $\delta^{13}C(CH_4)$, $\delta^{13}C(C_2H_6)$ and $\delta^{13}C(C_3H_8)$ were in the range of -43.8‰ ~ -33.1‰, -25.5‰ ~ -23.2 ‰ and -22.8‰ ~ -21.9‰, respectively (Nos. 38 - 51). For the Akita samples, $\delta^{13}C(CH_4)$, $\delta^{13}C(C_2H_6)$ and

Table 14   Oil field gases and their carbon isotopic ratios of methane, ethane and propane.

No. Location		$\delta^{13}C(CH_4)$ /‰	$\delta^{13}C(C_2H_6)$ /‰	$\delta^{13}C(C_3H_8)$ /‰
Akita				
23	Yabase-1*	-53.6	-27.0	-23.5
24	Yabase-2	-41.8	-29.1	-26.3
25	Yabase-3	-38.9	-26.7	-24.5
26	Yabase-4*	-45.0	-28.9	-25.8
27	Yabase-5*	-44.4	-26.6	-23.1
28	Yabase-6*	-50.3	-30.7	-27.0
29	Sarukawa-1*	-50.5	-33.0	-28.1
31	Sarukawa-3	-53.6	-32.6	-28.0
32	Sarukawa-4*	-56.4	-32.3	-28.1
34	Nishioogata-2*	-51.9	-30.1	-25.9
35	Fukumezawa*	-47.8	-30.2	-26.4
36	Yurihara-1*	-36.1	-25.6	-23.8
37	Yurihara-2*	-52.1	-27.0	-24.7
Niigata				
38	Mitsuke-1*	-35.5	-24.3	-22.7
39	Mitsuke-2*	-34.8	-23.4	-21.9
43	Higashiniigata-4*	-43.8	-23.5	-22.1
44	Higashiniigata-5*	-40.9	-23.2	-21.9
47	Yoshii*	-33.1	-24.4	-22.8
50	Kubiki-2*	-34.7	-25.5	-22.8
51	Kubiki-3	-38.2	NM	NM

NM not measured
* Igari (1999)

$\delta^{13}C(C_3H_8)$ were in the range of -56.4 ‰ ~ -36.4 ‰, -33.0 ‰ ~ -25.6 ‰ and -28.1 ‰ ~ -23.1 ‰, respectively (Nos. 23-37).

4.2.3 Discussion

The origins of oil field gases from Akita and Niigata are interpreted as a thermogenic gas or mixture of thermogenic and biogenic gases because they have low to intermediate $\delta^{13}C(CH_4)$ values (-56.4 ‰ ~ -33.1 ‰). This result does not conflict with the results of Sakata et al. (1986), and Waseda and Omokawa (1988).

Figure 27 shows that there is a strong correlation (r = 0.98) between the $\delta^{13}C(C_2H_6)$ and $\delta^{13}C(C_3H_8)$ values. By the method of least squares, the correlation given by the following equation:

$$\delta^{13}C(C_3H_8) = 0.662 \ \delta^{13}C(C_2H_6) - 6.44 \ ‰ \ (14)$$

After approximation of Eq. (14)

$$\delta^{13}C(C_3H_8) = (2/3) \ \delta^{13}C(C_2H_6) - (1/3)19.3 \ ‰. \ (15)$$

The thermogenic hydrocarbon is generally formed by decomposition of the source kerogen. According to Chung et al. (1988), the carbon isotopic ratios of hydrocarbon of n carbon atoms, $\delta^{13}C(C_nH_{2n+2})$, is expressed by the following equation:

$$n\delta^{13}C(C_nH_{2n+2})= (n-1) \delta^{13}C(source) + \delta^{13}C(terminal), \ (16)$$

where $\delta^{13}C(terminal)$ is the isotopic ratios of the terminal carbon that was originally bound to the source kerogen, and $\delta^{13}C(source)$ is the carbon isotopic ratios of the source kerogen. Chung et al. (1988) assumed that $\delta^{13}C(terminal)$ is smaller than $\delta^{13}C(source)$ because of the kinetic isotope effect in the breakdown of the C(terminal)-source bond. They also assumed that other hydrocarbons of n-1 carbon atoms whose carbon isotopic ratios are equal to $\delta^{13}C(source)$ are not affected by the kinetic isotope effect.
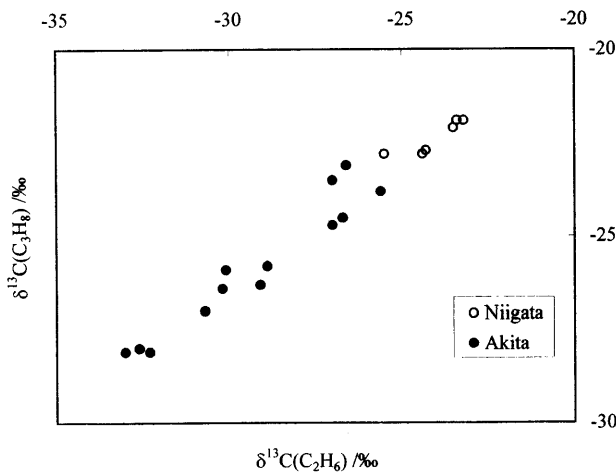
Equation (16) indicates that $\delta^{13}C(C_nH_{2n+2})$ is expressed as the weighted average of (n-1) carbon atoms, which have the same isotopic ratios as the source kerogen, and terminal carbon of $\delta^{13}C(terminal)$.

After rearrangement, and substituting 2 or 3 for n, the isotopic ratios for thermogenic ethane $\delta^{13}C(C_2H_6)$ and propane $\delta^{13}C(C_3H_8)$ are expressed as follows:

$$\delta^{13}C(C_2H_6)=(1/2) \delta^{13}C(source)+(1/2) \delta^{13}C(terminal) \ (17)$$

and

$$\delta^{13}C(C_3H_8)=(2/3) \delta^{13}C(source)+(1/3) \delta^{13}C(terminal). \ (18)$$

Assuming that an ethane-propane pair in a sample came from the same source kerogen and has the same $\delta^{13}C(terminal)$ (Chung et al., 1988), the relation between $\delta^{13}C(C_2H_6)$ and $\delta^{13}C(C_3H_8)$ is expressed as follows;

$$\delta^{13}C(C_3H_8)=(2/3) \delta^{13}C(C_2H_6)+(1/3) \delta^{13}C(source) \ (19)$$

Equation (15) for the Niigata and Akita samples accords with Eq. (19). This suggests that changes of $\delta^{13}C(C_2H_6)$ and $\delta^{13}C(C_3H_8)$ of oil field gases from Akita and Niigata were controlled kinetically and $\delta^{13}C(source)$ of the gases are close to each other (about -19.3 ‰).

The $\delta^{13}C$ of oil produced from oil and gas fields is shown in Table 15. It is known that $\delta^{13}C$ of kerogen and coexisting bitumen strongly correlate to each other (Shimoyama and Matsubaya, 1985), and that the difference between $\delta^{13}C$ of oil and source kerogen is only 0.5 ~ 3 ‰ (Omokawa, 1985). If fractionation between oil and source kerogen is 3 ‰, $\delta^{13}C$ of source kerogen in the studied area is inferred to be about -19.0 ~

Fig. 27 Relation between $\delta^{13}C (C_2H_6)$ and $\delta^{13}C (C_3H_8)$.

Table 15 Carbon isotopic ratios of oils.

Location		$\delta^{13}C(oil)$ /‰
Akita		
	Yabase	-23.7 **
	Sarukawa	-23.8 **
	Nishioogata	ND
	Fukumezawa	-23.7 **
	Yurihara	-22.0 ***
Niigata		
	Mitsuke	-23.8 **
	Higashiniigata	-22.4 *
	Yoshii	ND
	Kubiki	-23.4 **

ND: no data
*Omokawa(1985)
**Okada et al. (1989)
***Waseda and Omokawa (1990)

-20.8 ‰. This value does not conflict with the calculated source kerogen value (-19.3 ‰).

For the cleavage reaction of ^{12}C-source bond, rate constant k_{12} is expressed by the following equation:

$$k_{12} = A_{12}\exp(-E_{12}/RT), \quad (20)$$

where A_{12} is the frequency factor, R is the Boltzmann constant, E_{12} is the activation energy, and T is the reaction temperature.

For the cleavage reaction of ^{13}C-source bond, rate constant k_{13} is expressed by the following equation:

$$k_{13} = A_{13}\exp(-E_{13}/RT). \quad (21)$$

After rearrangement,

$$k_{13}/k_{12} = (A_{13}/A_{12})\exp((E_{12} - E_{13})/RT). \quad (22)$$

A_{12} and A_{13} are constants and it is known that $E_{12} < E_{13}$. Therefore, k_{13}/k_{12} or the kinetic effect (δ ^{13}C(terminal) - δ^{13}C(source)) would decrease with increasing generation temperature.

Calculated δ ^{13}C(terminal) - δ ^{13}C(source) of the samples are shown in Table 16. The values of the samples from Niigata are much smaller than those from Akita. This indicates that samples from Niigata were generated at higher temperatures than those from Akita. According to the reservoir temperatures shown in

Table 16   Calculated δ^{13}C (terminal) - δ^{13}C (source).

No. Location	Calculated δ^{13}C(terminal) - δ^{13}C(source) /‰
Akita	
23 Yabase-1	-21.0
24 Yabase-2	-16.8
25 Yabase-3	-13.2
26 Yabase-4	-18.6
27 Yabase-5	-21.0
28 Yabase-6	-22.2
29 Sarukawa-1	-29.4
31 Sarukawa-3	-27.6
32 Sarukawa-4	-25.2
34 Nishioogata-2	-25.2
35 Fukumezawa	-22.8
36 Yurihara-1	-10.8
37 Yurihara-2	-13.8
Niigata	
38 Mitsuke-1	-9.6
39 Mitsuke-2	-9.0
43 Higashiniigata-4	-8.4
44 Higashiniigata-5	-7.8
47 Yoshii	-9.6
50 Kubiki-2	-16.2
51 Kubiki-3	

Table 17   Reservoir temperatures.

Location	Reservoir temperature /°C	Median temperature /°C
Akita		
Yabase	38-97*	68
Sarukawa	45-89*	67
Nishioogata	39-53*	46
Fukumezawa	74-77*	76
Yurihara	30-100*	65
Niigata		
Mitsuke	83-90*	87
Higashiniigata	82-90*	86
Yoshii	119-131*	125
Kubiki	54-72*	63

*Akiba *et al.* (1992)

Table 17, the average of the median temperatures for Niigata (89 ℃) is higher than that for Akita (64 ℃). It is inferred that the generation temperatures of the gases from Niigata are higher than those from Akita. This conclusion does not conflict with the conclusion obtained from isotopic data.

There is only a weak correlation (r = 0.77) between δ ^{13}C(CH$_4$) and δ ^{13}C(C$_2$H$_6$) as shown in Fig. 28. Substituting n= 1 or 2 in Eq. (16) and after rearrangement,

$$\delta^{13}C(C_2H_6)=(1/2)\,\delta^{13}C(CH_4)+(1/2)\,\delta^{13}C(source) . \quad (23)$$

The calculated correlation line, when -19.3 ‰ is used for δ^{13}C(source) in Eq. (23), is also shown in Fig. 28. The measured values of δ^{13}C(CH$_4$) are lower than the calculated line by the magnitudes shown as the lengths of horizontal lines from the data points in the figure. This indicates all the samples are thermogenic gas mixed with biogenic gas that has low δ ^{13}C(CH$_4$) value
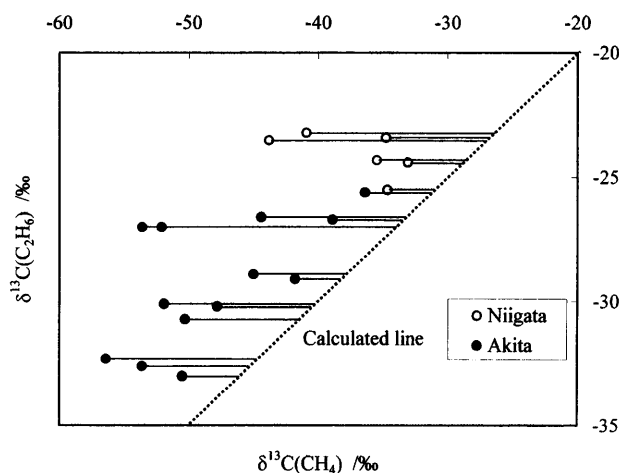

Fig. 28   Relation between δ^{13}C (CH$_4$) and δ^{13}C (C$_2$H$_6$).

(about -67 ‰ in Japan (Nakai *et al.*, 1974)) and little nonmethane hydrocarbons.

The mixing ratios of thermogenic gas and biogenic gas as for methane can be calculated as follows when the $\delta^{13}C(CH_4)$ value of biogenic gas is assumed to be -67 ‰.

Substituting 1 for n in Eq. (16)

$$\delta^{13}C(CH_4)calc = \delta^{13}C(terminal) . (24)$$

By rearrangement of Eqs. (16) and (17),

$$\delta^{13}C(C_2H_6)=(1/2)\,\delta^{13}C(source)+(1/2)\,\delta^{13}C(CH_4)calc \quad (25)$$

and

$$\delta^{13}C(C_3H_8)=(2/3)\,\delta^{13}C(source)+(1/3)\,\delta^{13}C(CH_4)calc. \quad (26)$$

After rearrangement of Eqs. (25) and (26),

$$\delta^{13}C(CH_4)calc = 4\,\delta^{13}C(C_3H_8) - 3\,\delta^{13}C(C_2H_6). \quad (27)$$

Mixing ratio of biogenic gas and thermogenic gas as approximated by methane is calculated by

$$x = (\,\delta^{13}C(CH_4)calc - \delta^{13}C(CH_4)measured) / (67 + \delta^{13}C(CH_4)calc), \quad (28)$$

where, x is the mixing ratio of biogenic gas as approximated by methane, $\delta^{13}C(CH_4)calc$ is the $\delta^{13}C(CH_4)$ value calculated by Eq. (27), $\delta^{13}C(CH_4)measured$: measured $\delta^{13}C(CH_4)$ value. The mixing ratios of biogenic gas as approximated by methane are 3 to 55% (Table 18). This shows that almost all the gases from Akita and Niigata have been mixed with biogenic gas.

Table 18　Mixing ratios of biogenic gas and thermogenic gas (CH_4).

	$\delta^{13}C(CH_4)$ /‰	thermogenic /%	biogenic /%
Akita			
23 Yabase-1	-53.6	45	55
24 Yabase-2	-41.8	85	15
25 Yabase-3	-38.9	83	17
26 Yabase-4	-45.0	76	24
27 Yabase-5	-44.4	76	24
28 Yabase-6	-50.3	66	34
29 Sarukawa-1	-50.5	85	15
31 Sarukawa-3	-53.6	65	35
32 Sarukawa-4	-56.4	48	52
34 Nishioogata-2	-51.9	62	38
35 Fukumezawa	-47.8	76	24
36 Yurihara-1	-36.4	85	15
37 Yurihara-2	-52.1	45	55
Niigata			
38 Mitsuke-1	-35.5	83	17
39 Mitsuke-2	-34.8	82	18
43 Higashi-Niigata-4	-43.8	59	41
44 Higashi-Niigata-5	-40.9	65	35
47 Yoshii	-33.1	90	10
50 Kubiki-2	-34.7	97	3

5.　Summary and conclusions

Hydrocarbon compositions including neopentane, which has been rarely measured, of major natural gases in Japan are examined. It is inferred that the decomposition by hydrogen abstraction is a major factor of the hydrocarbon composition of natural gases.

The compositional change of natural gases due to migration was examined by a simulation experiment using gas chromatograph. It was found that fractionation by clay minerals or zeolites is insignificant under normal subsurface conditions where these minerals are hydrated.

The $\delta^{13}C(CH_4)$ values of dissolved-in-water type gases distinguish the origins of the gases; biogenic, thermogenic or mixed origin of both types.

The $\delta^{13}C(CH_4)$, $\delta^{13}C(C_2H_6)$ and $\delta^{13}C(C_3H_8)$ values for oil field gases in Niigata and Akita, suggest that almost all the samples are of mixed origin of thermogenic and biogenic gases. The proportion of biogenic gases ranging from 3 to 55% as approximated by methane was estimated using the isotopic values.

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日本の主要なガス田より産する天然ガスの有機地球化学的研究

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要　旨

これまでにほとんど測定例の無いネオペンタンを含む日本の天然ガスの軽質炭化水素組成を測定した．エタン/プロパン比，ネオペンタン/イソペンタン比，ネオペンタン/イソブタン比の対数間には直線関係が観察された．この関係は，水素引き抜きによる炭化水素の分解によるものと説明された．

移動に伴う，軽質炭化水素の分別作用に対する岩石種の効果について研究を行った．種々の岩石や，鉱物を充填したカラムを用いたガスクロマトグラフィーにより，それぞれの炭化水素の保持時間を測定した．メタン，エタン，プロパン，イソブタン，n-ブタン，イソペンタン，n-ペンタンについて測定を行った．層間水を持つ粘土鉱物，及びゼオライトを用いた場合に分別が観察された．それぞれの炭化水素の保持時間の順番は粘土鉱物やゼオライトの種類に依存した．また，鉱物の空焼き時間の増加とともに分別は大きくなり，空焼きなしでは，非常に小さい分別が観察されるのみだった．これらのことは，分別には粘土鉱物やゼオライトの水が抜けた層間や細孔が重要であり，鉱物が水和している通常の地下条件下では粘土鉱物やゼオライトによる，炭化水素の分別は重要でない事が明らかになった．

日本の水溶性ガス田の天然ガスのメタンの炭素同位体比を測定した．その結果，これまで一般に水溶性天然ガスは微生物起源と考えられてきたが，熱分解起源のものも存在することが明らかになった．

秋田・新潟の油田ガスのメタン・エタン・プロパンの炭素同位体比を測定した．エタンの炭素同位体比とプロパンの炭素同位体比の間には強い相関が観察された．この相関は速度論的に説明可能だった．一方メタンとエタンの炭素同位体比の間には弱い相関が観察されるのみだった．これは微生物起源ガスの混入の影響と推定された．さらに，これらの同位体比を用いることにより，熱分解ガスと微生物起源ガスの混合率を計算することができ，秋田・新潟の油田ガスは，ほとんどが両者の混合ガスであることが明らかになった．