

Organic Geochemical  
Study of Major Natural Gases  
in Japanese Gas Fields

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# Organic Geochemical Study of Major Natural Gases in Japanese Gas Fields

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## Chapter 1.

### General Introduction



### *Types of natural gases*

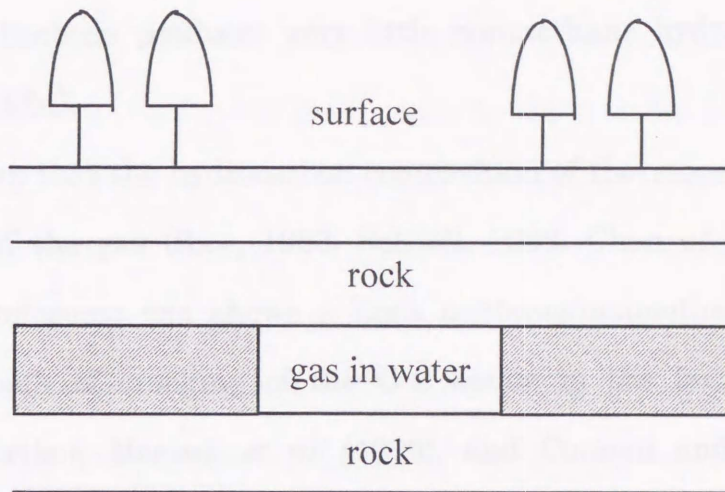
Natural gases in gas fields are classified into two types by their origins: biogenic and thermogenic gases (Fuex, 1977; Schoell, 1983). The biogenic gases are produced from CO<sub>2</sub> in sediments by bacterial reduction or from organic matter in sediments by bacterial decomposition. The thermogenic 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).

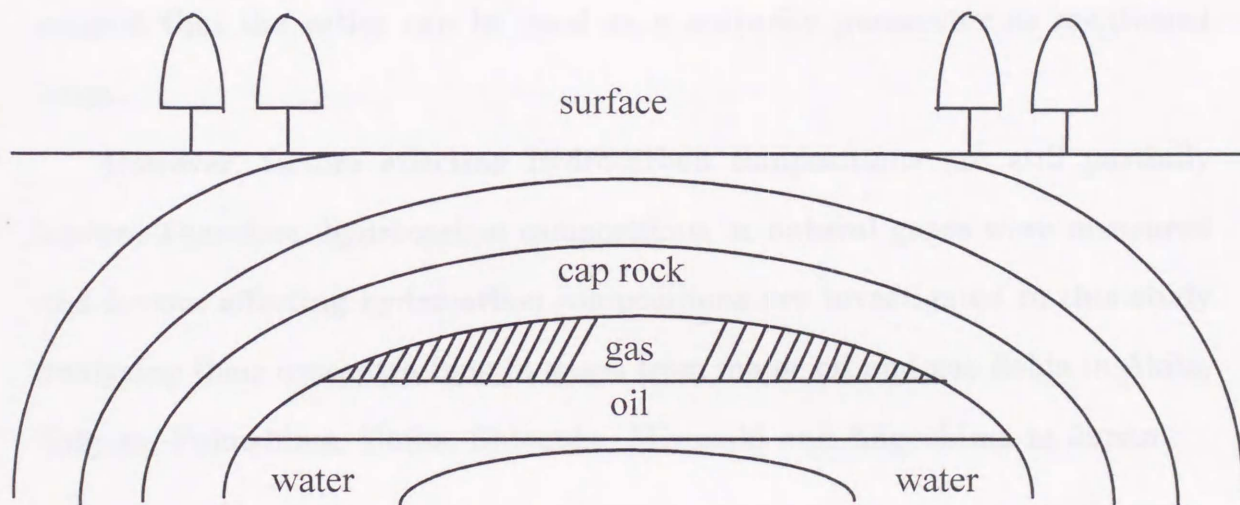
### *Factors affecting hydrocarbon compositions*

The main components in natural gas are hydrocarbons. 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 few nonmethane hydrocarbons (Schoell, 1983; Noble and Henk, 1998). The trace nonmethane hydrocarbons



*Dissolved-in-water type gas*



*Oil field gas*

Fig. 1-1. Types of gas fields

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 (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 gases from Niigata correlate with  $\delta^{13}\text{C}(\text{CH}_4)$ , and suggest that the ratios can be used as a maturity parameter as mentioned below.

However, factors affecting hydrocarbon compositions are still 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.

#### *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 compositions 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.

#### *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  $\delta^{13}\text{C}(\text{CH}_4)$  values (about  $-25 \sim -45$  ‰) (Stahl, 1974; Shoell, 1983, 1988). On the other hand, biogenic gases contain little nonmethane hydrocarbons and show low  $\delta^{13}\text{C}(\text{CH}_4)$  values (about

-60 ~ -70 ‰) (Rice and Claypool, 1981). Mixed gases of both types have intermediate nonmethane hydrocarbon concentrations and  $\delta^{13}\text{C}(\text{CH}_4)$  values. Further, it is considered that magmatic gas shows very high  $\delta^{13}\text{C}(\text{CH}_4)$  value (about -15 ‰) (Welhan and Craig, 1981).

Nakai (1960) and Nakai *et al.* (1972) 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 Kusakata 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.

#### *Carbon isotopic ratios of oil field gases*

For understanding of the origins of natural gases,  $\delta^{13}\text{C}(\text{CH}_4)$  is usually measured. Further, maturity of thermogenic gas is estimated from  $\delta^{13}\text{C}(\text{CH}_4)$  (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  $\delta^{13}\text{C}(\text{CH}_4)$  values. Determination of thermogenic gas maturity is difficult because  $\delta^{13}\text{C}(\text{CH}_4)$  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  $\delta^{13}\text{C}(\text{C}_2\text{H}_6)$  and  $\delta^{13}\text{C}(\text{C}_3\text{H}_8)$  of oil field gases in Niigata and Akita were measured and the factors determining those values were evaluated.

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Factor affecting hydrocarbon compositions of natural

## Chapter 2.

Factor affecting hydrocarbon compositions of natural  
gases.

## Summary

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 in natural gases.

## Introduction

The main components in natural gases are hydrocarbons. There have been several reports on the hydrocarbon composition of Japanese natural gases. Sakata *et al.* (1986), and Waseda and Omokawa (1988) measured hydrocarbon compositions in gases from the Akita and Niigata oil fields. Yonetani (1963) measured the hydrocarbon compositions of dissolved-in-water type gases.

The main component in natural gas hydrocarbons is methane. It is known that the concentrations of nonmethane hydrocarbons in natural gas depend on their origin. Thermogenic gas shows relatively high concentrations of nonmethane hydrocarbons than biogenic gas (Schoell, 1983). Trace nonmethane hydrocarbons contained in biogenic gas are considered to be of thermogenic origin, because the bacteria produces very little nonmethane hydrocarbons (Davis and Squires; 1954).

For thermogenic gas, it is known that the nonmethane hydrocarbon concentration depends on maturity (Schoell, 1983) and a type of kerogen (Rice, 1983). Highly matured gas shows a low nonmethane hydrocarbon concentration as a result of cracking of C-C bonds in larger hydrocarbon molecules. Furthermore, Heroux *et al.* (1979) and Connan and Cassou (1980) showed the isobutane/*n*-butane ratio depends on the maturity. As for gases in Japan, Kato (1989) showed the ratio correlates well with maturity; high maturity gas shows a high isobutane/*n*-butane ratio. 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. Thus, factors affecting the hydrocarbon composition are only partially known. Therefore, hydrocarbon compositions are measured and factor affecting hydrocarbon compositions of natural gases is considered for gases from gas fields in Akita, Niigata, Fukushima, Chiba, Shizuoka, Miyazaki and Kagoshima.

## 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. 2-3). 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 a 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 2-1).

For dissolved-in-water type gases, the measured hydrocarbons are in a

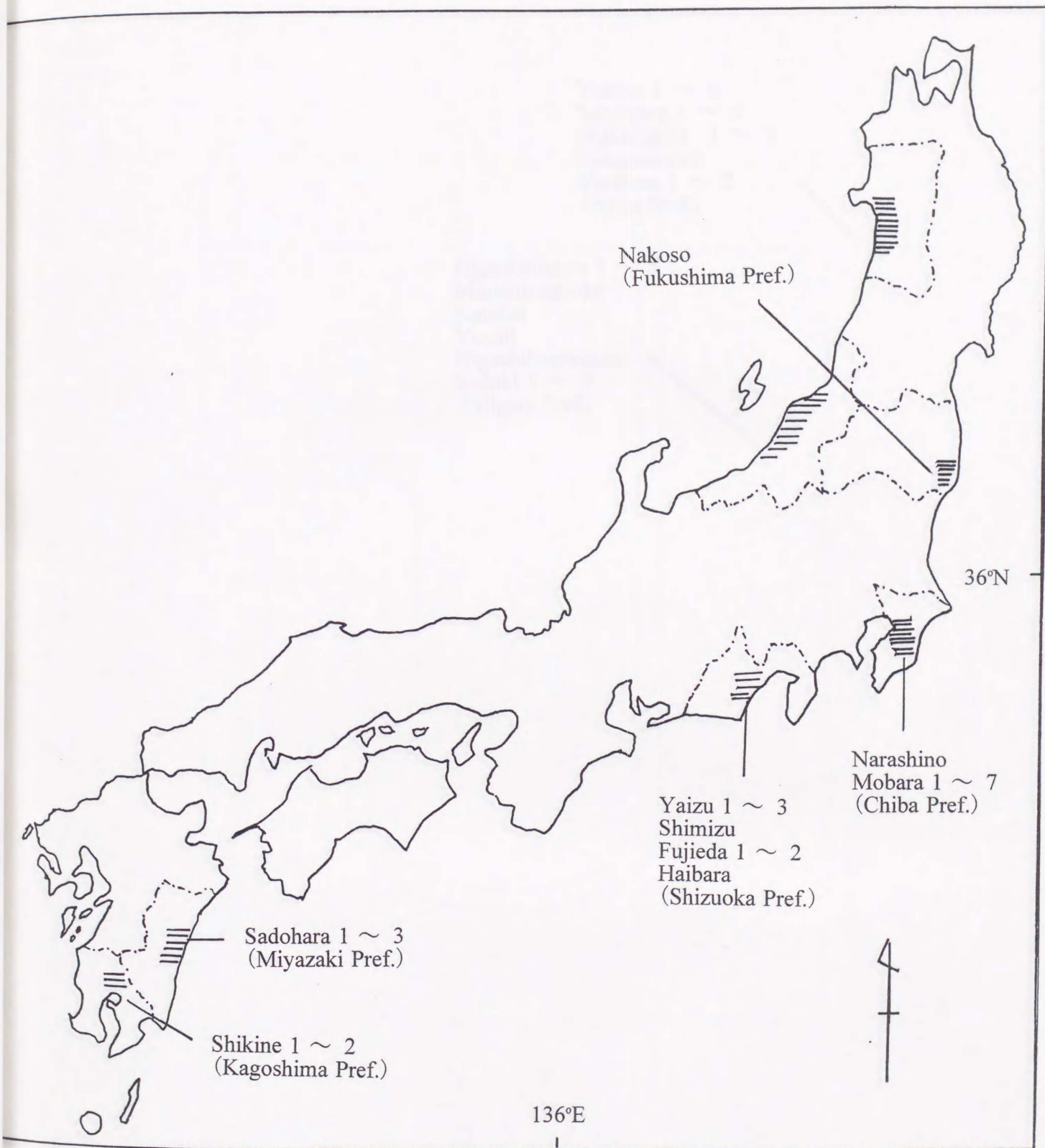


Fig. 2-1 Sampling sites of dissolved-in-water type gases

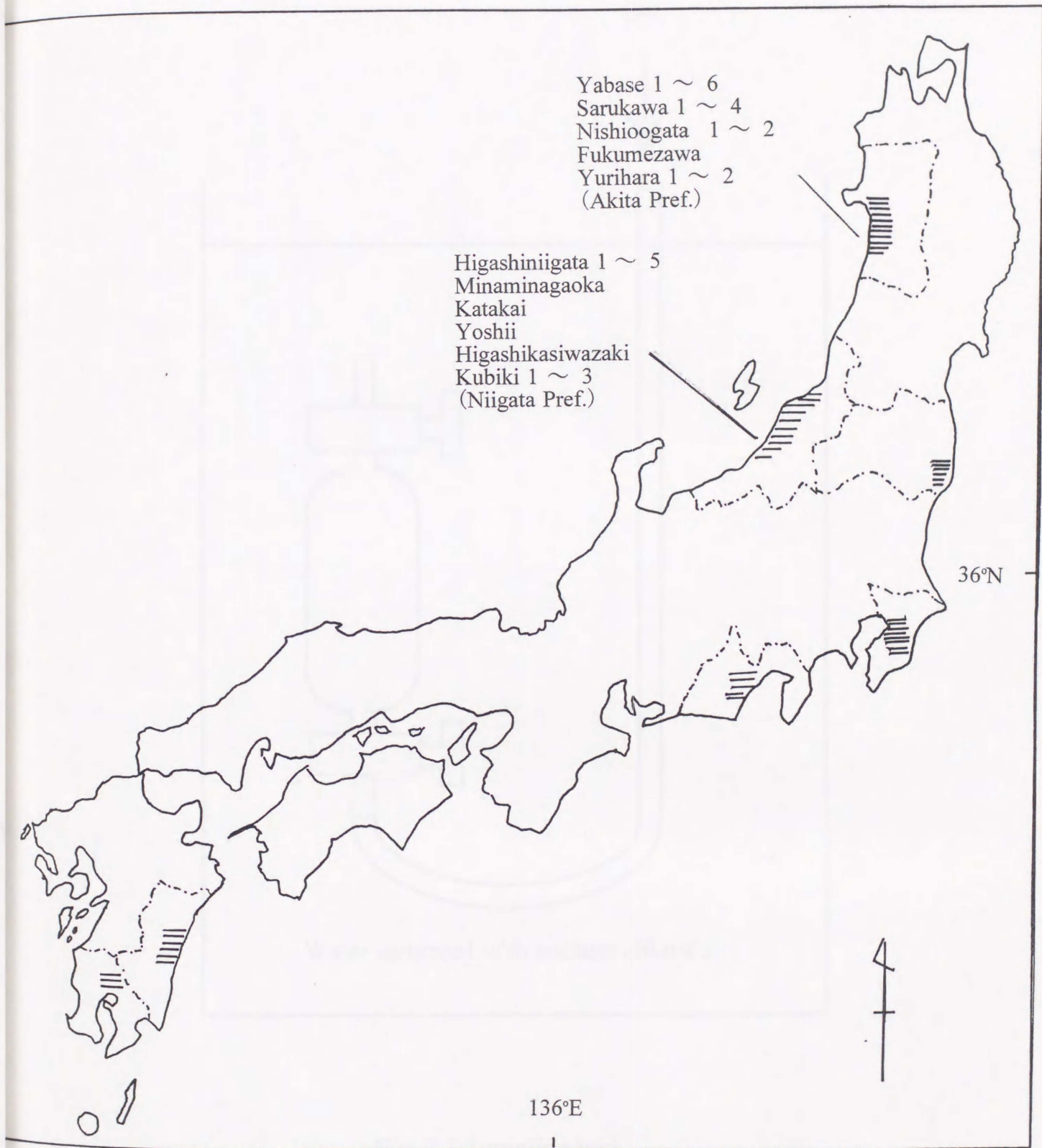


Fig. 2-2 Sampling sites of oil field gases



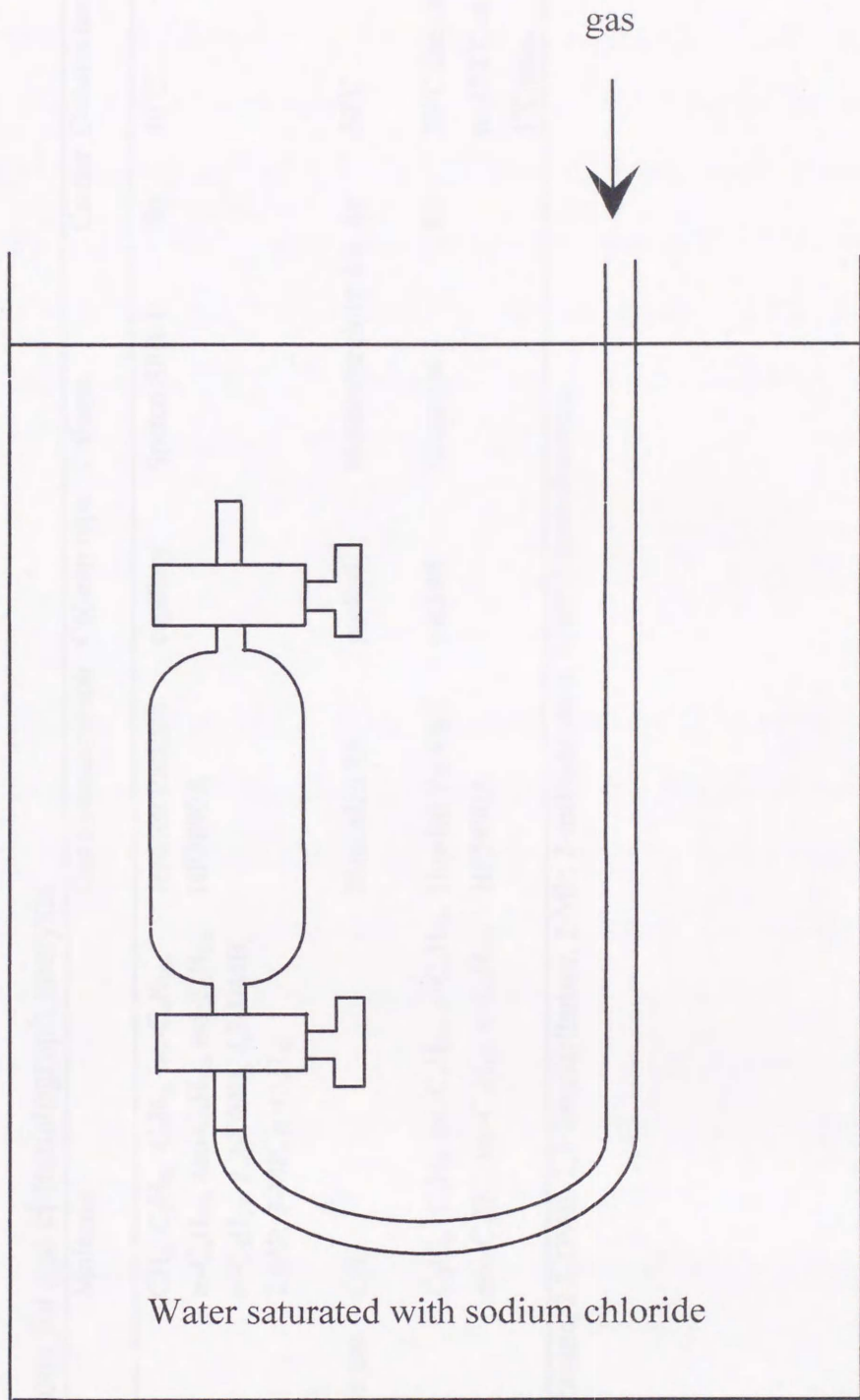


Fig. 2-3 Sampling tool

Table 2-1 Conditions for gas chromatograph analysis

| Gas field type              | Molecule   | Gas chromatograph          | Column type | Column             | Carrier | Column temperature                                       |
|-----------------------------|--|----------------------------|-------------|--------------------|---------|--|
| Oil field gas               | CH <sub>4</sub> , C <sub>2</sub> H <sub>6</sub> , C <sub>3</sub> H <sub>8</sub> , iso-C <sub>4</sub> H <sub>10</sub> ,<br><i>n</i> -C <sub>4</sub> H <sub>10</sub> , neo-C <sub>5</sub> H <sub>12</sub> , iso-C <sub>5</sub> H <sub>12</sub> ,<br><i>n</i> -C <sub>5</sub> H <sub>12</sub> , 2,2-DMB, 2,3-DMB,<br>2-MP, 3-MP, <i>n</i> -C <sub>6</sub> H <sub>12</sub> | Hewlett Packard<br>HP5890A | capillary   | Spelco SPB-1       | He      | 40°C   |
| Dissolved-in-water type gas | CH <sub>4</sub>  | Shimadzu 8A                | packed      | Molecular sieve 5A | Ar      | 50°C   |
|                             | C <sub>2</sub> H <sub>6</sub> , C <sub>3</sub> H <sub>8</sub> , iso-C <sub>4</sub> H <sub>10</sub> , <i>n</i> -C <sub>4</sub> H <sub>10</sub> ,<br>neo-C <sub>5</sub> H <sub>12</sub> , iso-C <sub>5</sub> H <sub>12</sub> , <i>n</i> -C <sub>5</sub> H <sub>12</sub>  | Hewlett Packard<br>HP5890A | packed      | Silica gel         | He      | 70°C then increased<br>to 120°C at a rate of<br>1°C/min. |

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

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 °C, column temperature: 50 °C). 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 °C, column temperature: initially 70 °C then increased to 120 °C at a rate of 1 °C/min.) (Table 2-1).

## Results

A gas chromatogram of an oil field gas (Sarukawa-3) is shown in Fig. 2-4. Gas chromatograms of dissolved-in-water type gas (Yaizu-2) are shown in Figs. 2-5 and 2-6. For the oil field gas samples, CH<sub>4</sub> is in the range of 55.7 ~ 95.9 %. CH<sub>4</sub> is the main component. C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>, iso-C<sub>4</sub>H<sub>10</sub>, *n*-C<sub>4</sub>H<sub>10</sub>, neo-C<sub>5</sub>H<sub>12</sub>, iso-C<sub>5</sub>H<sub>12</sub> and *n*-C<sub>5</sub>H<sub>12</sub> are in the range of 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 2-2. 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<sub>6</sub>H<sub>14</sub> is 23 ~ 85 ppm, 69 ~ 1230 ppm, 120 ~ 1760 ppm, 70 ~ 1170 ppm and 60 ~ 1350 ppm, respectively as shown in Table 2-3. For the dissolved-in-water type gas samples, CH<sub>4</sub> is in the range of 49.3 ~ 95.0 %. CH<sub>4</sub> is the main component. C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>, iso-C<sub>4</sub>H<sub>10</sub>, *n*-C<sub>4</sub>H<sub>10</sub>, neo-C<sub>5</sub>H<sub>12</sub>,

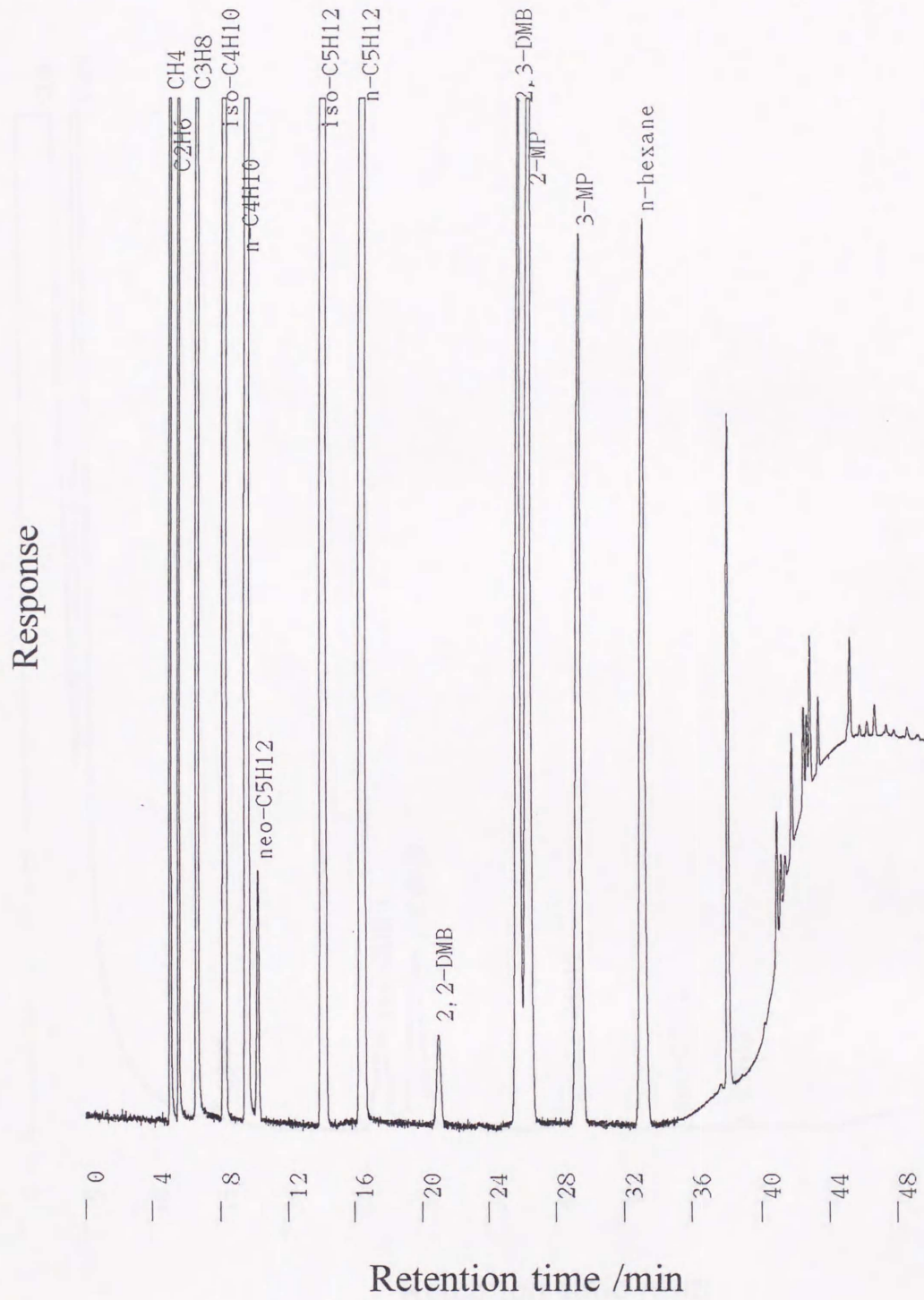


Fig. 2-4 Gas chromatogram of oil field gas (Sarukawa-3)

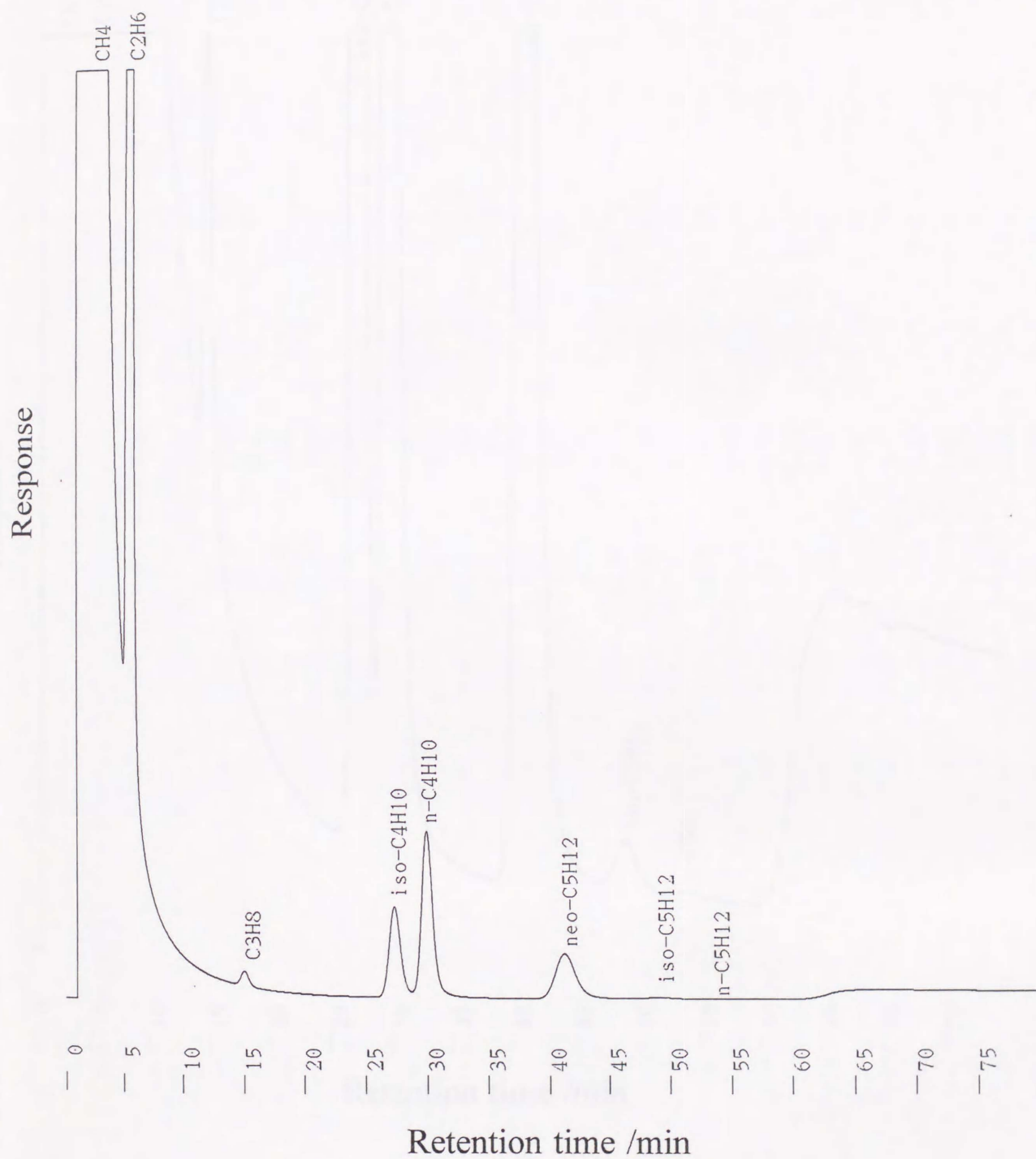


Fig. 2-5 Gas chromatogram of dissolved-in-water type gas (Yaizu-2)

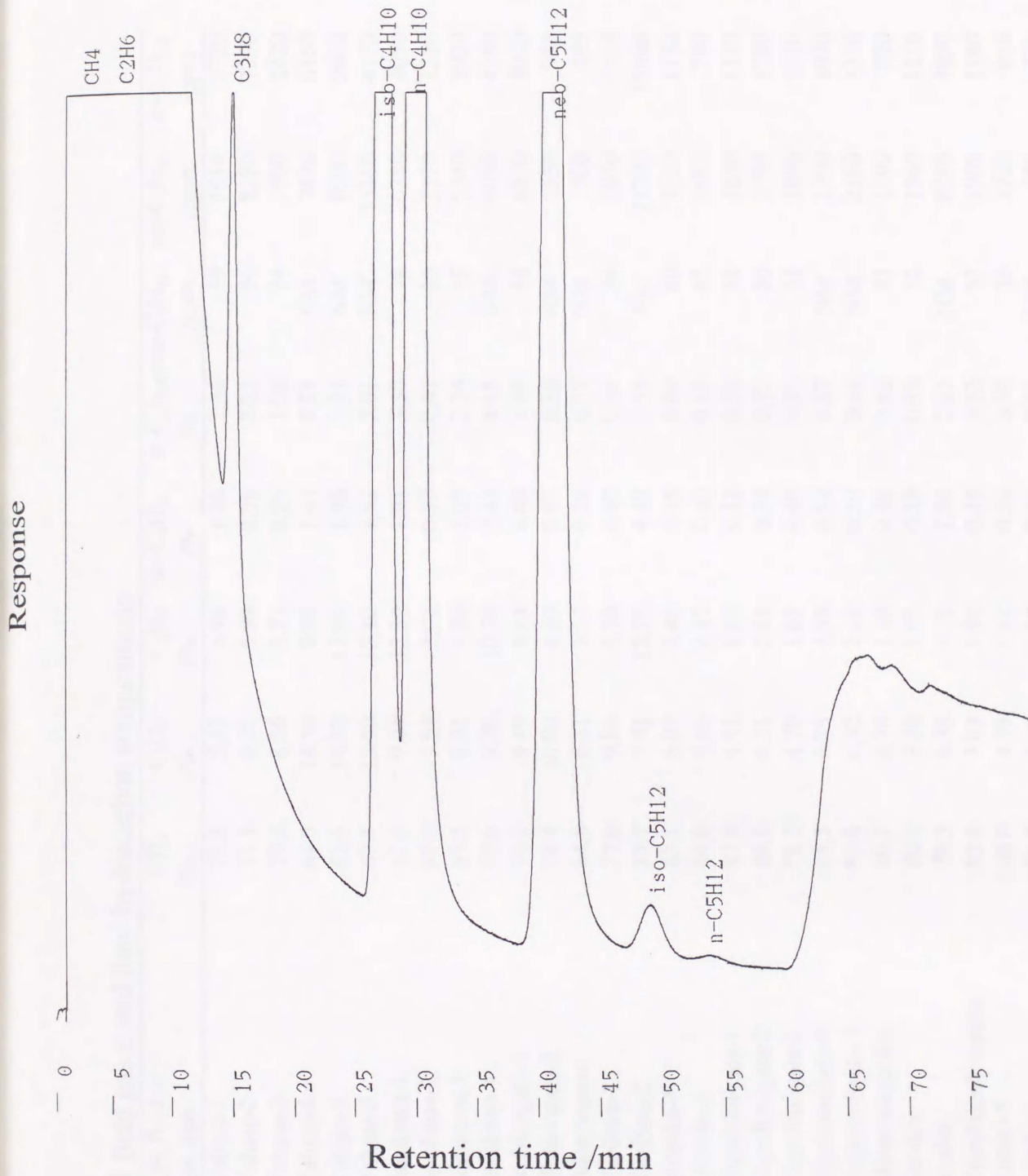


Fig. 2-6 Gas chromatogram of dissolved-in-water type gas (Yaizu-2, enlarged)

Table 2-2 Oil field gases and their hydrocarbon compositions

| No. | Gas field or<br>gas sign | CH <sub>4</sub><br>/% | C <sub>2</sub> H <sub>6</sub><br>/% | C <sub>3</sub> H <sub>8</sub><br>/% | iso-C <sub>4</sub> H <sub>10</sub><br>/% | n-C <sub>4</sub> H <sub>10</sub><br>/% | neo-C <sub>5</sub> H <sub>12</sub><br>/ppm | iso-C <sub>5</sub> H <sub>12</sub><br>/ppm | n-C <sub>5</sub> H <sub>12</sub><br>/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

Table 2-3 Oil field gases and their hexane isomer concentrations

| No. | Gas field or<br>gas sign | 2,2-DMB<br>(ppm) | 2,3-DMB<br>(ppm) | 2-MP<br>(ppm) | 3-MP<br>(ppm) | <i>n</i> -C <sub>6</sub> H <sub>12</sub><br>(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



iso-C<sub>5</sub>H<sub>12</sub> and *n*-C<sub>5</sub>H<sub>12</sub> 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, as shown in Table 2-4.. They show relatively low concentrations.

## Discussion

The relation between the ratios of C<sub>2</sub>H<sub>6</sub>/C<sub>3</sub>H<sub>8</sub> and that of neo-C<sub>5</sub>H<sub>12</sub>/iso-C<sub>5</sub>H<sub>12</sub> is shown in Fig. 2-7. The relation between the ratio of C<sub>2</sub>H<sub>6</sub>/C<sub>3</sub>H<sub>8</sub> and that of neo-C<sub>5</sub>H<sub>12</sub>/iso-C<sub>4</sub>H<sub>10</sub> is shown in Fig. 2-8. The relation between the ratio of neo-C<sub>5</sub>H<sub>12</sub>/iso-C<sub>5</sub>H<sub>12</sub> and that of neo-C<sub>5</sub>H<sub>12</sub>/iso-C<sub>4</sub>H<sub>10</sub> is shown in Fig. 2-9. A log-log straight line correlation is observed between the ratios. There are three possible explanations for the log-log straight line correlations in Figs. 2-7, 2-8 and 2-9. They are 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

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<sub>4</sub>H<sub>10</sub>/*n*-C<sub>4</sub>H<sub>10</sub> ratio increases with a progression of bacterial degradation. If the bacterial oxidation affects the neo-C<sub>5</sub>H<sub>12</sub>/iso-C<sub>5</sub>H<sub>12</sub>, neo-C<sub>5</sub>H<sub>12</sub>/iso-C<sub>4</sub>H<sub>10</sub> and C<sub>2</sub>H<sub>6</sub>/C<sub>3</sub>H<sub>8</sub> ratios, it is expected that the ratios show straight line correlation with the iso-C<sub>4</sub>H<sub>10</sub>/*n*-C<sub>4</sub>H<sub>10</sub> ratio.

Table 2-4 Dissolved-in-water type gases and their hydrocarbon compositions

| No.             | Gas field or<br>gas sign | CH <sub>4</sub><br>/% | C <sub>2</sub> H <sub>6</sub><br>/ppm | C <sub>3</sub> H <sub>8</sub><br>/ppm | iso-C <sub>4</sub> H <sub>10</sub><br>/ppm | n-C <sub>4</sub> H <sub>10</sub><br>/ppm | neo-C <sub>5</sub> H <sub>12</sub><br>/ppm | iso-C <sub>5</sub> H <sub>12</sub><br>/ppm | n-C <sub>5</sub> H <sub>12</sub><br>/ppm |
|-----------------|--------------------------|-----------------------|---------------------------------------|---------------------------------------|--|--|--|--|--|
| 1 <sup>1)</sup> | Nakoso                   | 93.7                  | 120                                   | 0.75                                  | 0.058                                      | 0.042                                    | 0.16                                       | 0.053                                      | 0.032                                    |
| 2 <sup>1)</sup> | 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                                       |

<sup>1)</sup> 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

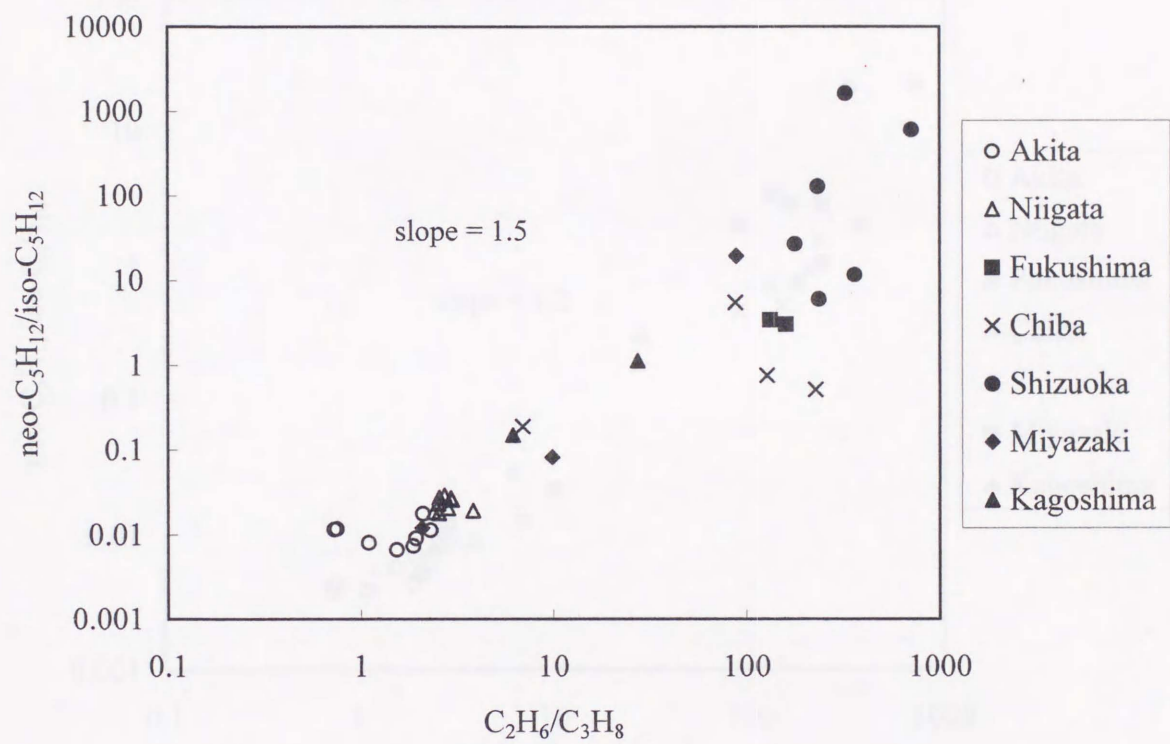


Fig. 2-7 Cross-plot of  $C_2H_6/C_3H_8$  and  $neo-C_5H_{12}/iso-C_5H_{12}$

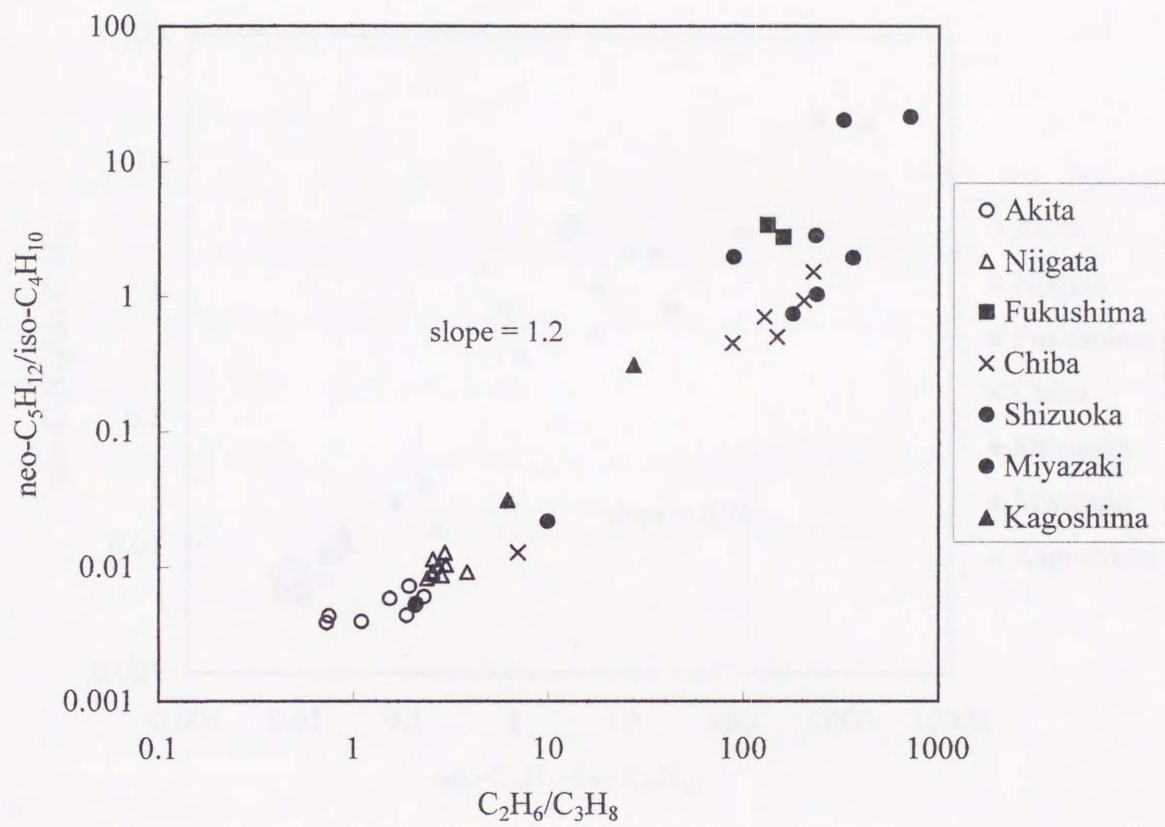


Fig. 2-8 Cross-plot of  $C_2H_6/C_3H_8$  and  $neo-C_5H_{12}/iso-C_4H_{10}$

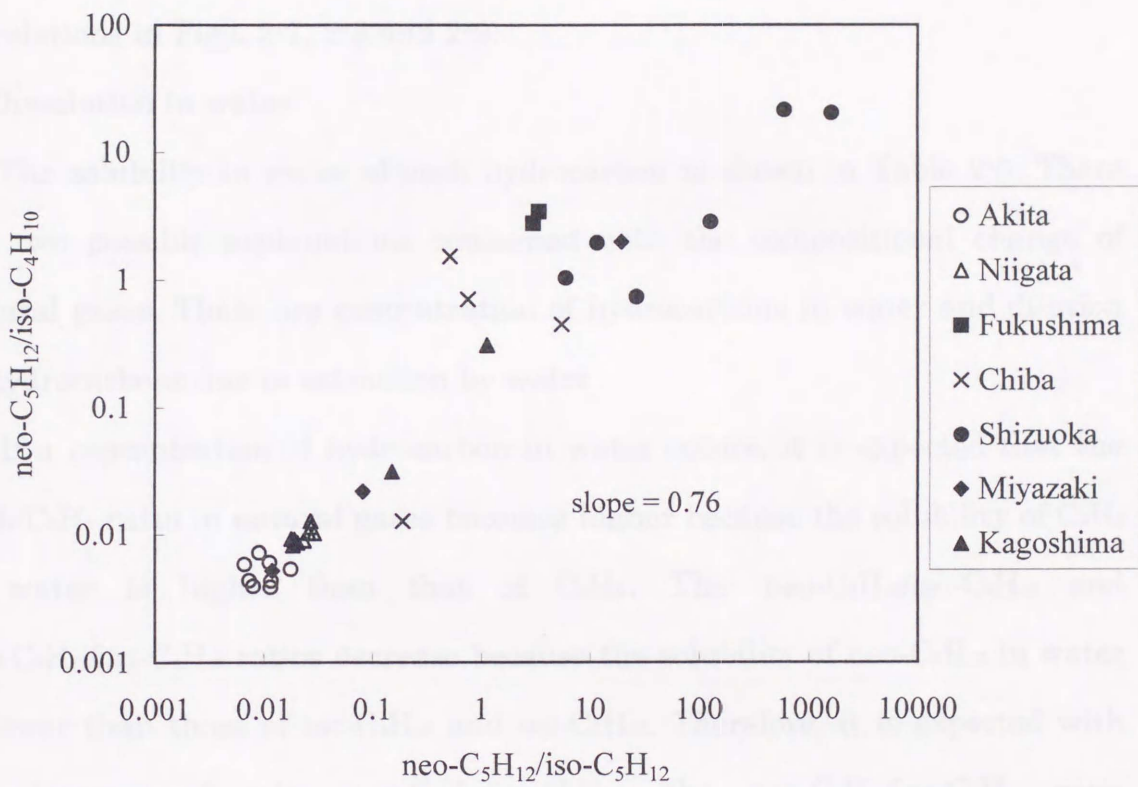


Fig. 2-9 Cross-plot of neo-C<sub>5</sub>H<sub>12</sub>/iso-C<sub>5</sub>H<sub>12</sub> and neo-C<sub>5</sub>H<sub>12</sub>/iso-C<sub>4</sub>H<sub>10</sub>

The relation between neo-C<sub>5</sub>H<sub>12</sub>/iso-C<sub>5</sub>H<sub>12</sub> and iso-C<sub>4</sub>H<sub>10</sub>/*n*-C<sub>4</sub>H<sub>10</sub>, neo-C<sub>5</sub>H<sub>12</sub>/iso-C<sub>4</sub>H<sub>10</sub> and iso-C<sub>4</sub>H<sub>10</sub>/*n*-C<sub>4</sub>H<sub>10</sub> and C<sub>2</sub>H<sub>6</sub>/C<sub>3</sub>H<sub>8</sub> and iso-C<sub>4</sub>H<sub>10</sub>/*n*-C<sub>4</sub>H<sub>10</sub> are shown in Figs. 2-10, 2-11 and 2-12, respectively. The neo-C<sub>5</sub>H<sub>12</sub>/iso-C<sub>5</sub>H<sub>12</sub>, neo-C<sub>5</sub>H<sub>12</sub>/iso-C<sub>4</sub>H<sub>10</sub> and C<sub>2</sub>H<sub>6</sub>/C<sub>3</sub>H<sub>8</sub> ratios do not show straight line correlation with the iso-C<sub>4</sub>H<sub>10</sub>/*n*-C<sub>4</sub>H<sub>10</sub> ratio. Therefore, it is concluded that bacterial degradation is not a major factor affecting the log-log straight line correlations in Figs. 2-7, 2-8 and 2-9.

## 2) Dissolution in water

The solubility in water of each hydrocarbon is shown in Table 2-5. There are two possible explanations concerned with the compositional change of natural gases. These are 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<sub>2</sub>H<sub>6</sub>/C<sub>3</sub>H<sub>8</sub> ratio in natural gases becomes higher because the solubility of C<sub>2</sub>H<sub>6</sub> in water is higher than that of C<sub>3</sub>H<sub>8</sub>. The neo-C<sub>5</sub>H<sub>12</sub>/iso-C<sub>5</sub>H<sub>12</sub> and neo-C<sub>5</sub>H<sub>12</sub>/iso-C<sub>4</sub>H<sub>10</sub> ratios decrease because the solubility of neo-C<sub>5</sub>H<sub>12</sub> in water is lower than those of iso-C<sub>4</sub>H<sub>10</sub> and iso-C<sub>5</sub>H<sub>12</sub>. Therefore, it is expected with the increase of ratio neo-C<sub>5</sub>H<sub>12</sub>/iso-C<sub>5</sub>H<sub>12</sub>, the neo-C<sub>5</sub>H<sub>12</sub>/iso-C<sub>4</sub>H<sub>10</sub> ratio increases. This agrees with Fig. 2-15. With the increase of ratio C<sub>2</sub>H<sub>6</sub>/C<sub>3</sub>H<sub>8</sub>, the ratios neo-C<sub>5</sub>H<sub>12</sub>/iso-C<sub>5</sub>H<sub>12</sub> and neo-C<sub>5</sub>H<sub>12</sub>/iso-C<sub>4</sub>H<sub>10</sub> decrease. This does not agree with Figs. 2-13 and 2-14. Therefore, the concentration of hydrocarbons in water is not considered as a major factor affecting the log-log straight line correlations in Figs. 2-7, 2-8 and 2-9.

If the dilution of hydrocarbons due to extraction by water occurs, the C<sub>2</sub>H<sub>6</sub>/C<sub>3</sub>H<sub>8</sub> ratio in natural gases becomes lower because the solubility of C<sub>2</sub>H<sub>6</sub>

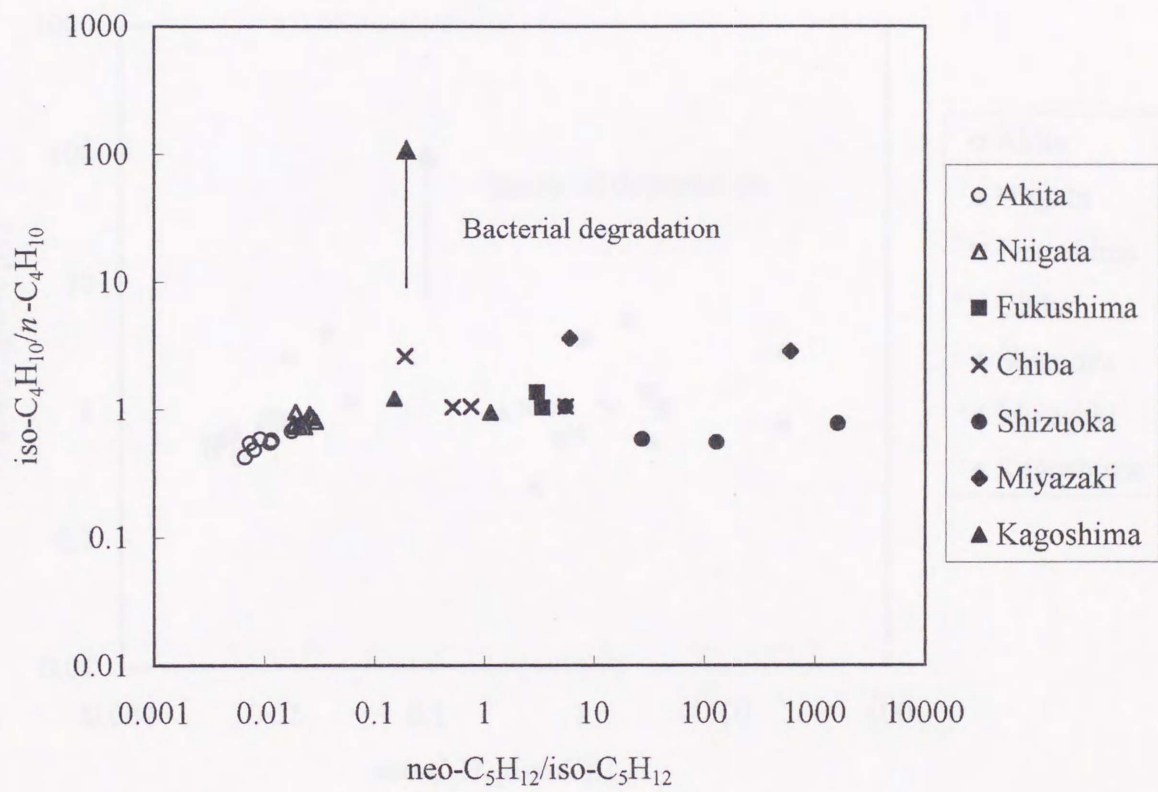


Fig. 2-10 Cross-plot of neo-C<sub>5</sub>H<sub>12</sub>/iso-C<sub>5</sub>H<sub>12</sub> and iso-C<sub>4</sub>H<sub>10</sub>/n-C<sub>4</sub>H<sub>10</sub>

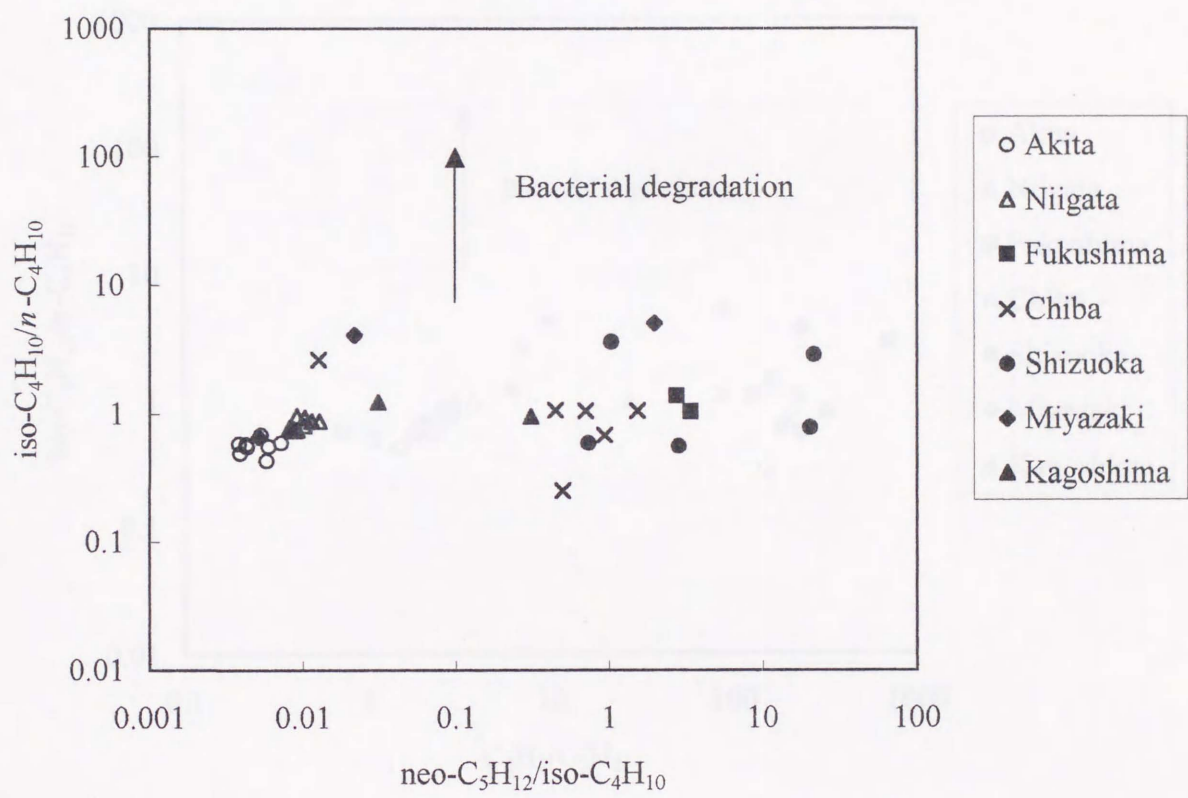


Fig. 2-11 Cross-plot of neo-C<sub>5</sub>H<sub>12</sub>/iso-C<sub>4</sub>H<sub>10</sub> and iso-C<sub>4</sub>H<sub>10</sub>/n-C<sub>4</sub>H<sub>10</sub>



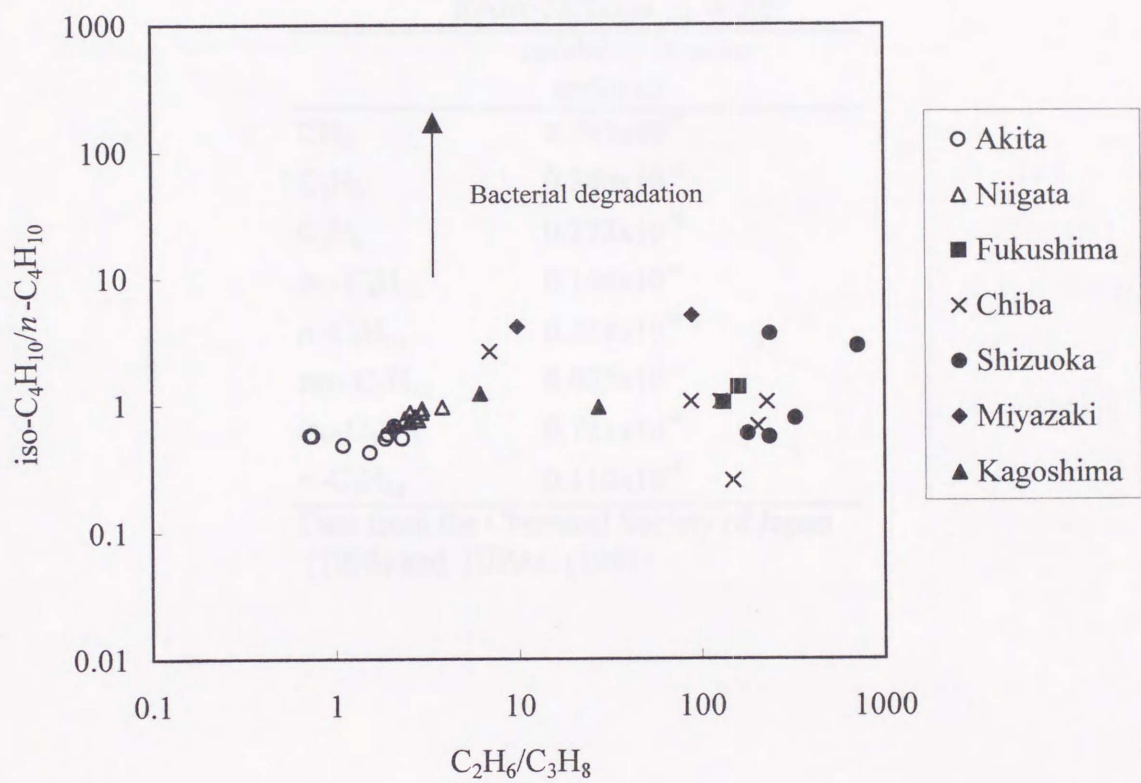


Fig. 2-12 Cross-plot of  $\text{C}_2\text{H}_6/\text{C}_3\text{H}_8$  and  $\text{iso-C}_4\text{H}_{10}/n\text{-C}_4\text{H}_{10}$

Table 2-5 Solubility of hydrocarbons in water

|  | solubility in water<br>mol/mol |
|--|--------------------------------|
| CH <sub>4</sub>                          | 0.253x10 <sup>-4</sup>         |
| C <sub>2</sub> H <sub>6</sub>            | 0.340x10 <sup>-4</sup>         |
| C <sub>3</sub> H <sub>8</sub>            | 0.273x10 <sup>-4</sup>         |
| iso-C <sub>4</sub> H <sub>10</sub>       | 0.146x10 <sup>-4</sup>         |
| <i>n</i> -C <sub>4</sub> H <sub>10</sub> | 0.224x10 <sup>-4</sup>         |
| neo-C <sub>5</sub> H <sub>12</sub>       | 0.083x10 <sup>-4</sup>         |
| iso-C <sub>5</sub> H <sub>12</sub>       | 0.121x10 <sup>-4</sup>         |
| <i>n</i> -C <sub>5</sub> H <sub>12</sub> | 0.110x10 <sup>-4</sup>         |

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

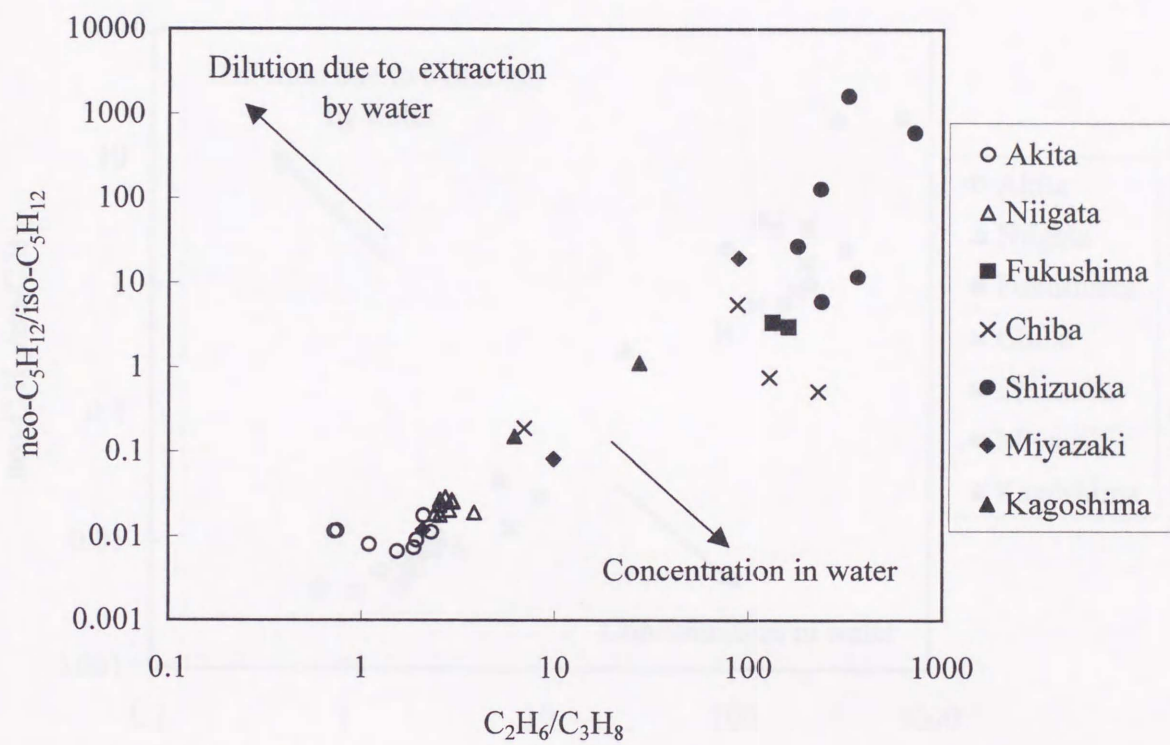


Fig. 2-13 Cross-plot of  $C_2H_6/C_3H_8$  and  $neo-C_5H_{12}/iso-C_5H_{12}$   
(Dissolution in water)

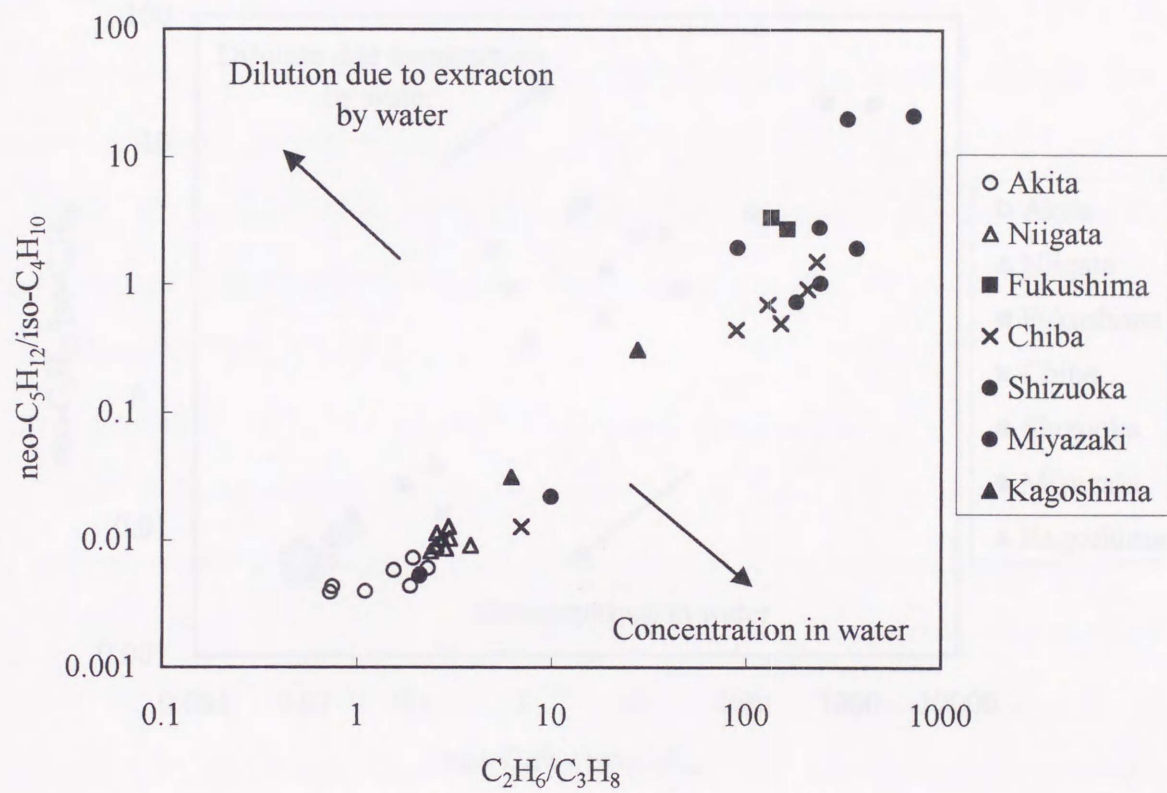


Fig. 2-14 Cross-plot of  $\text{C}_2\text{H}_6/\text{C}_3\text{H}_8$  and  $\text{neo-C}_5\text{H}_{12}/\text{iso-C}_4\text{H}_{10}$   
(Dissolution in water)

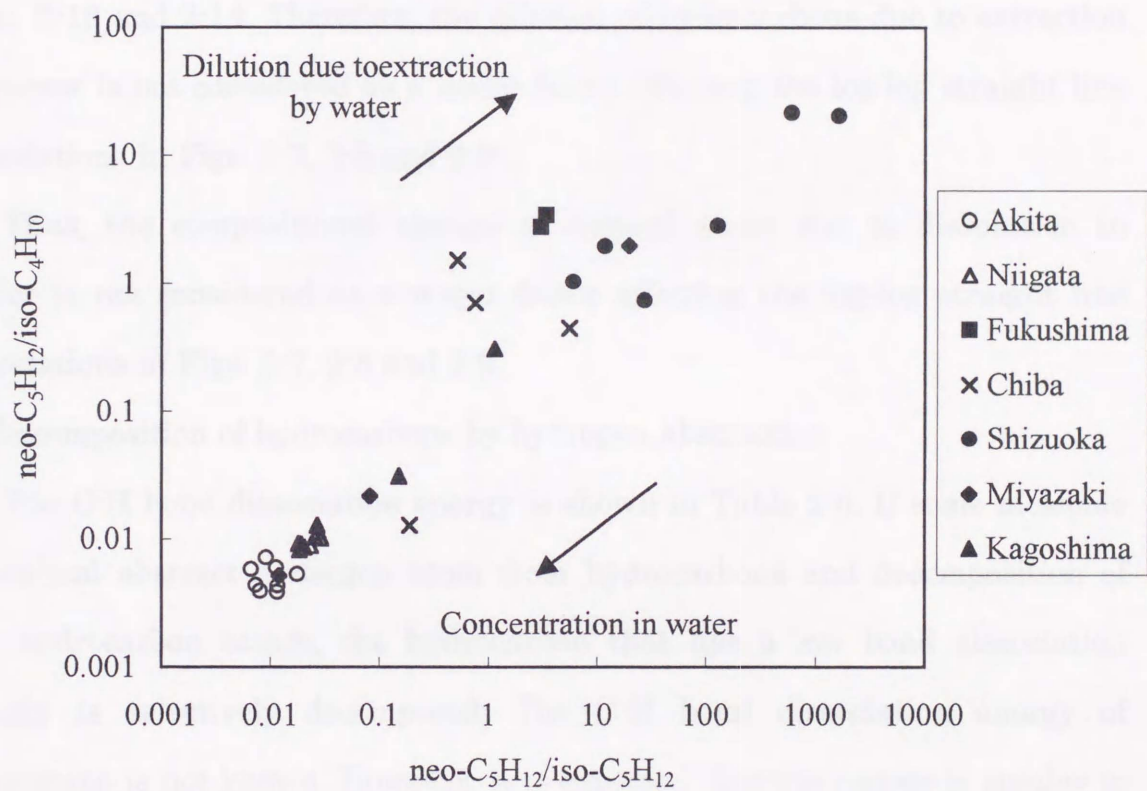


Fig. 2-15 Cross-plot of  $\text{neo-C}_5\text{H}_{12}/\text{iso-C}_5\text{H}_{12}$  and  $\text{neo-C}_5\text{H}_{12}/\text{iso-C}_4\text{H}_{10}$  (Dissolution in water)

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 with the decrease of ratio  $neo-C_5H_{12}/iso-C_5H_{12}$ , ratio  $neo-C_5H_{12}/iso-C_4H_{10}$  decreases. This agrees with Fig. 2-15. 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. 2-13 and 2-14. 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. 2-7, 2-8 and 2-9.

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. 2-7, 2-8 and 2-9.

### 3) Decomposition of hydrocarbons by hydrogen abstraction

The C-H bond dissociation energy is shown in Table 2-6. 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 explained in Figs. 2-16, 2-17 and 2-18.

A radical that is expected to abstract hydrogen from a hydrocarbon is the hydroxyl radical. The decomposition reaction of hydrocarbons by the

Table 2-6 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)

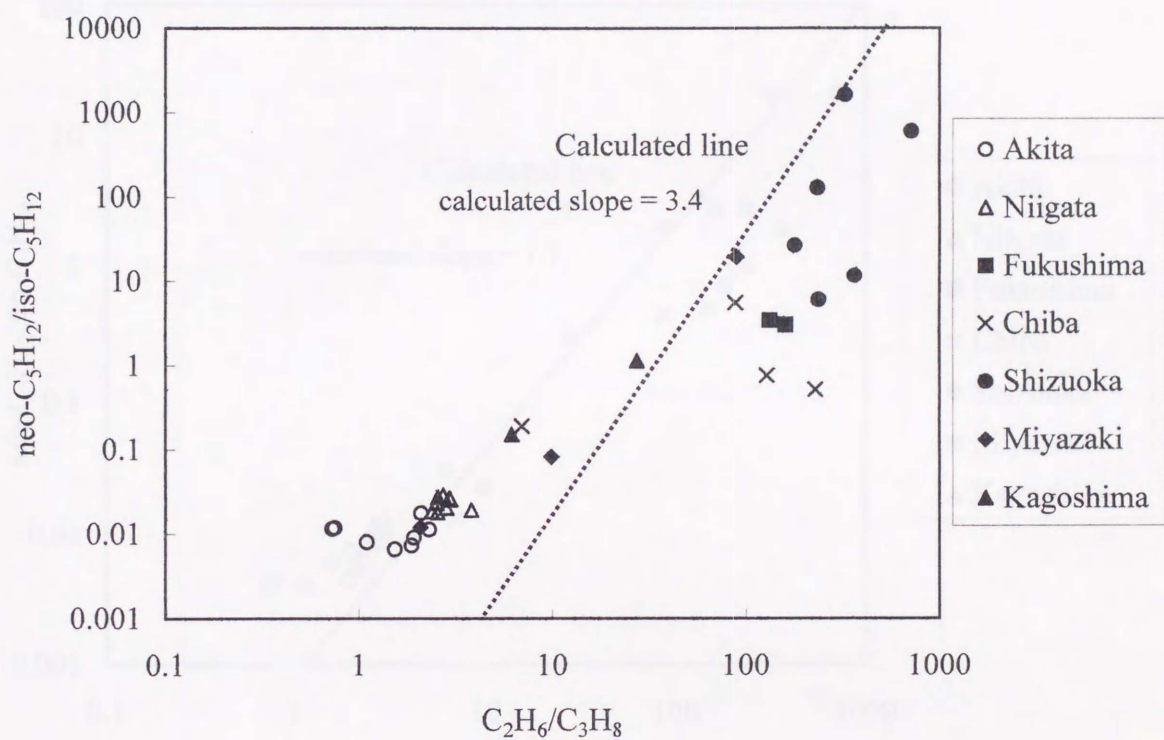


Fig. 2-16 Cross-plot of  $C_2H_6/C_3H_8$  and  $neo-C_5H_{12}/iso-C_5H_{12}$   
(Decomposition by H abstraction)



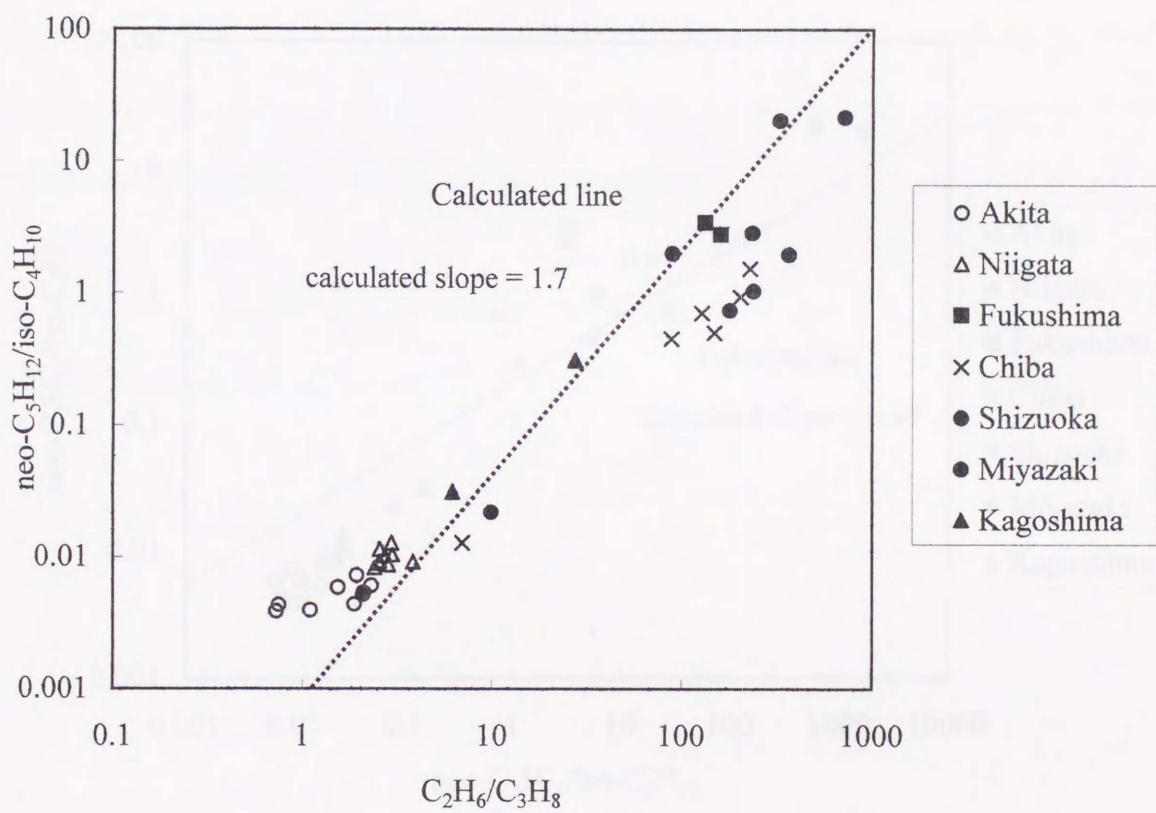


Fig. 2-17 Cross-plot of  $C_2H_6/C_3H_8$  and  $neo-C_5H_{12}/iso-C_4H_{10}$   
(Decomposition by H abstraction)

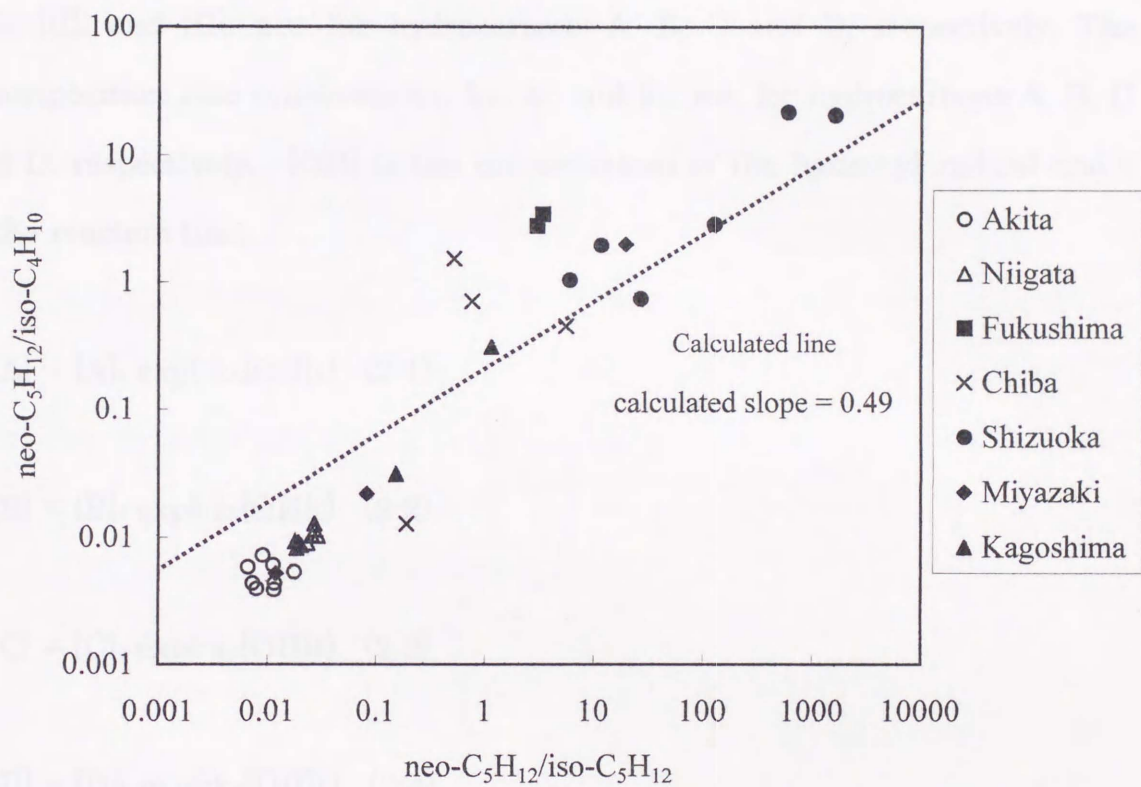


Fig. 2-18 Cross-plot of neo-C<sub>5</sub>H<sub>12</sub>/iso-C<sub>5</sub>H<sub>12</sub> and neo-C<sub>5</sub>H<sub>12</sub>/iso-C<sub>4</sub>H<sub>10</sub> (Decomposition by H abstraction)

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. (2-1), (2-2), (2-3) and (2-4). In Eqs. (2-1), (2-2), (2-3) and (2-4), [A], [B], [C] and [D] are the concentrations of hydrocarbons A, B, C and D, respectively. The initial concentrations of [A]<sub>0</sub>, [B]<sub>0</sub>, [C]<sub>0</sub> and [D]<sub>0</sub> are for hydrocarbons A, B, C and D, respectively. The decomposition rate constants k<sub>A</sub>, k<sub>B</sub>, k<sub>C</sub> and k<sub>D</sub> are for hydrocarbons A, B, C and D, respectively. [OH] is the concentration of the hydroxyl radical and t is the reaction time.

$$[A] = [A]_0 \exp(-k_A[OH]t) \quad (2-1)$$

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

$$[C] = [C]_0 \exp(-k_C[OH]t) \quad (2-3)$$

$$[D] = [D]_0 \exp(-k_D[OH]t) \quad (2-4)$$

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

$$\ln[A] = \ln[A]_0 - k_A[OH]t \quad (2-5)$$

$$\ln[B] = \ln[B]_0 - k_B[OH]t \quad (2-6)$$

$$\ln[C] = \ln[C]_0 - k_c[OH]t \quad (2-7)$$

$$\ln[D] = \ln[D]_0 - k_d[OH]t \quad (2-8)$$

From Eqs. (2-5) and (2-6),

$$\ln[A]/[B] - \ln[A]_0/[B]_0 = -(k_A - k_B)[OH]t \quad (2-9)$$

From Eqs. (2-7) and (2-8),

$$\ln[C]/[D] - \ln[C]_0/[D]_0 = -(k_c - k_d)[OH]t \quad (2-10)$$

From Eqs. (2-9) and (2-10)

$$\log([A]/[B]) = M \log([C]/[D]) + N \quad (2-11)$$

Where

$$M = (k_A - k_B)/(k_c - k_d) \quad (2-12)$$

$$N = \log([A]_0/[B]_0) - M \log([C]_0/[D]_0) \quad (2-13)$$

Eq. (2-11) means there is a straight line relation between the  $\log([A]/[B])$  and  $\log([C]/[D])$ . The slope is M which can be calculated from Eq. (2-12). The relative rate constant of the hydrocarbon decomposition reaction by hydroxyl

radicals in gas phases is shown in Table 2-7 (Atkinson, 1990). Calculated lines are shown in Figs. 2-16, 2-17 and 2-18. These lines are in accordance with measured results. If the decomposition occurs in the liquid phase, or other radicals or molecules abstract H atoms, it is expected that a similar calculated line is obtained, because the hydrocarbon decomposition rate is governed by the hydrocarbon 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. 2-7, 2-8 and 2-9, the two samples from Fukushima are the same sample. One sample is analyzed 6 days after the sampling and the other sample is analyzed 2 years after the sampling. The difference between the two samples in Figs. 2-7, 2-8 and 2-9 is not observed. Therefore, degradation of the samples under a preservation condition can be ignored.

Table 2-7 Relative rate constants for the reaction  
of OH radicals with alkanes

| Alkane                                   | Relative rate constants |      |      |      |
|--|-------------------------|------|------|------|
|  | 298K                    | 350K | 400K | 450K |
| CH <sub>4</sub>                          | 1                       | 3    | 5    | 10   |
| C <sub>2</sub> H <sub>6</sub>            | 32                      | 56   | 86   | 123  |
| C <sub>3</sub> H <sub>8</sub>            | 138                     | 194  | 257  | 330  |
| iso-C <sub>4</sub> H <sub>10</sub>       | 280                     | 336  | 398  | 453  |
| <i>n</i> -C <sub>4</sub> H <sub>10</sub> | 304                     | 381  | 465  | 558  |
| neo-C <sub>5</sub> H <sub>12</sub>       | 102                     | 154  | 215  | 286  |
| iso-C <sub>5</sub> H <sub>12</sub>       | 467                     | ND   | ND   | ND   |
| <i>n</i> -C <sub>5</sub> H <sub>12</sub> | 471                     | 581  | 702  | 835  |

Calculated from data by Atkinson (1990)

ND: no data

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### Chapter 3.

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

## Summary

Effect of rock types on the fractionation of light hydrocarbons in natural gases during migration in 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 examination were  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_3\text{H}_8$ , *iso*- $\text{C}_4\text{H}_{10}$ , *n*- $\text{C}_4\text{H}_{10}$ , *iso*- $\text{C}_5\text{H}_{12}$  and *n*- $\text{C}_5\text{H}_{12}$ .

The fractionation occurred when the sample was expandable clay minerals or zeolites. The order of retention times depended on the kind of clay minerals or zeolites. When montmorillonite, halloysite, vermiculite and mordenite were used, the order was  $\text{CH}_4 < \text{C}_2\text{H}_6 < \text{C}_3\text{H}_8 < \textit{iso}\text{-C}_4\text{H}_{10} < \textit{n}\text{-C}_4\text{H}_{10} < \textit{iso}\text{-C}_5\text{H}_{12} < \textit{n}\text{-C}_5\text{H}_{12}$ . When clinoptilolite was used, the order was  $\text{CH}_4 < \textit{iso}\text{-C}_4\text{H}_{10} < \text{C}_2\text{H}_6 < \textit{iso}\text{-C}_5\text{H}_{12} < \text{C}_3\text{H}_8 < \textit{n}\text{-C}_4\text{H}_{10}$ .

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 underground conditions where these minerals are hydrated.

## Introduction

The hydrocarbon compositions of natural gases is an important parameter for the consideration of their origin and maturity. However, this consideration can not be made easily because of possible changes in the natural gas composition during migration. Leythaeuser *et al.* (1979, 1980, 1982, 1983) and Whelan *et al.* (1984) analyzed hydrocarbon compositions of adsorbed gases in rocks, 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. In these simulations, many factors affected the fractionation of the hydrocarbons during migration. These factors are existence of water, porosity, permeability, rock type etc. To understand the general rule for hydrocarbon fractionation in rocks, the effect of sediment type must be known. Therefore, simulation experiments were performed using gas chromatography (GC).

## Experiments

### *Samples*

Samples used in the simulation experiments are listed in Table 3-1. 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

Table 3-1 Samples used for GC column packing

| No.   | Location                                  | Contained clay minerals or zeolite |
|---|---|------------------------------------|
| 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)                 | nd                                 |
| 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

or zeolites were determined by a X-ray diffractometer (CuK $\alpha$ , 40 kV, 150 mA).

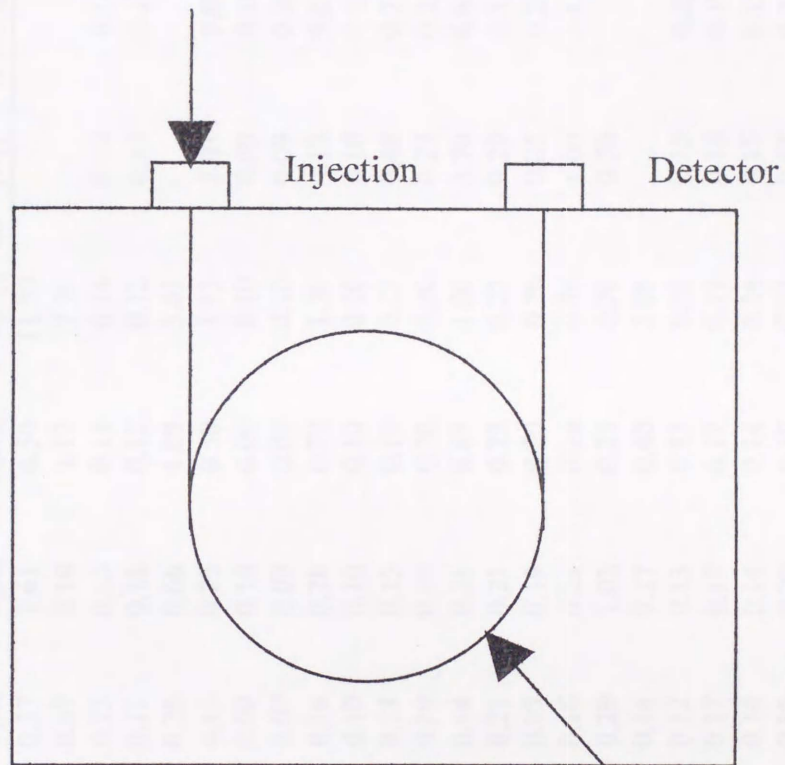
### *Simulation experiments*

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 a FID detector. The columns were preheated for 0 to 20 h at 90 °C, passing helium gas. The column temperature was then maintained at 50 °C. One  $\mu$ l 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. 3-1).

### 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 3-2. Under the conditions used in this examination, the retention times of methane were 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 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  $\text{CH}_4 < \text{iso-C}_4\text{H}_{10} < \text{C}_2\text{H}_6 < \text{iso-C}_5\text{H}_{12} < \text{C}_3\text{H}_8 < n\text{-C}_4\text{H}_{10}$ . When No. 23

CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>, iso-C<sub>4</sub>H<sub>10</sub>, *n*-C<sub>4</sub>H<sub>10</sub>, iso-C<sub>5</sub>H<sub>12</sub> and *n*-C<sub>5</sub>H<sub>12</sub>



Gas chromatograph

Stainless column packed with a single kind of or a various kinds of rocks and minerals

Fig. 3-1 Simulation experiment

Table 3-2 Retention times of hydrocarbons on GC columns packed with various rock and mineral samples with fixed aging period (18 or 20 hours)

| No.* | Flow rate<br>of carrier<br>gas (ml/min.) | Aging<br>time<br>/h | Retention time /min |                               |                               |                                    |  |                                    |  |  |
|------|--|---------------------|---------------------|-------------------------------|-------------------------------|------------------------------------|--|------------------------------------|--|--|
|      |  |                     | CH <sub>4</sub>     | C <sub>2</sub> H <sub>6</sub> | C <sub>3</sub> H <sub>8</sub> | iso-C <sub>4</sub> H <sub>10</sub> | <i>n</i> -C <sub>4</sub> H <sub>10</sub> | iso-C <sub>5</sub> H <sub>12</sub> | <i>n</i> -C <sub>5</sub> H <sub>12</sub> |  |
| 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                                     |  |

was used, the order was  $\text{iso-C}_4\text{H}_{10} = \text{iso-C}_5\text{H}_{12} < \text{CH}_4 < \text{C}_2\text{H}_6 < \text{C}_3\text{H}_8 < n\text{-C}_4\text{H}_{10}$ .

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 3-3. 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  $\text{CH}_4$  in Nos. 11, 13, 16, 17 and 18, and  $\text{C}_2\text{H}_6$  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  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_3\text{H}_8$ ,  $\text{iso-C}_4\text{H}_{10}$  and  $n\text{-C}_4\text{H}_{10}$ , its chromatogram is shown in Fig. 3-2.

## 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. The retention times of the hydrocarbons are listed in Table 3-2 where main constituents of the source rocks and reservoir 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 3-1). This result indicates



Table 3-3 Retention times of hydrocarbons on GC column packed with various mineral samples with various aging periods (0-20 h)

| Clay mineral<br>or zeolite        | Aging time<br>/h | Retention time /min. |                               |                               |                                    |                                  |                                    |                                  |
|-----------------------------------|------------------|----------------------|-------------------------------|-------------------------------|------------------------------------|----------------------------------|------------------------------------|----------------------------------|
|                                   |                  | CH <sub>4</sub>      | C <sub>2</sub> H <sub>6</sub> | C <sub>3</sub> H <sub>8</sub> | iso-C <sub>4</sub> H <sub>10</sub> | n-C <sub>4</sub> H <sub>10</sub> | iso-C <sub>5</sub> H <sub>12</sub> | n-C <sub>5</sub> H <sub>12</sub> |
| No. 11                            | 0.0              | 0.13                 | 0.13                          | 0.13                          | 0.14                               | 0.15                             | 0.20                               | 0.29                             |
| Montmorillonite<br>(Clay mineral) | 0.5              | 0.13                 | 0.13                          | 0.15                          | 0.20                               | 0.24                             | 0.52                               | 0.78                             |
|                                   | 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<br>(Clay mineral)            | 0.5              | 0.19                 | 0.19                          | 0.19                          | 0.20                               | 0.20                             | 0.22                               | 0.22                             |
|                                   | 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<br>(Clay mineral)      | 0.5              | 0.11                 | 0.13                          | 0.24                          | 0.65                               | 0.98                             | 3.76                               | 6.79                             |
|                                   | 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<br>(Clay mineral)        | 0.5              | 0.20                 | 0.21                          | 0.21                          | 0.23                               | 0.24                             | 0.31                               | 0.35                             |
|                                   | 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<br>(Clay mineral)        | 0.5              | 0.19                 | 0.19                          | 0.19                          | 0.20                               | 0.20                             | 0.23                               | 0.24                             |
|                                   | 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<br>(Clay mineral)     | 0.5              | 0.14                 | 0.15                          | 0.19                          | 0.25                               | 0.41                             | 0.73                               | 1.93                             |
|                                   | 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<br>(Zeolite)       | 0.5              | 0.09                 | 0.13                          | 0.30                          | 0.19                               | 1.76                             | 0.55                               |                                  |
|                                   | 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<br>(Zeolite)            | 0.5              | 0.09                 | 0.10                          | 0.11                          | 0.11                               | 0.27                             |                                    |                                  |
|                                   | 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                             |                                    |                                  |

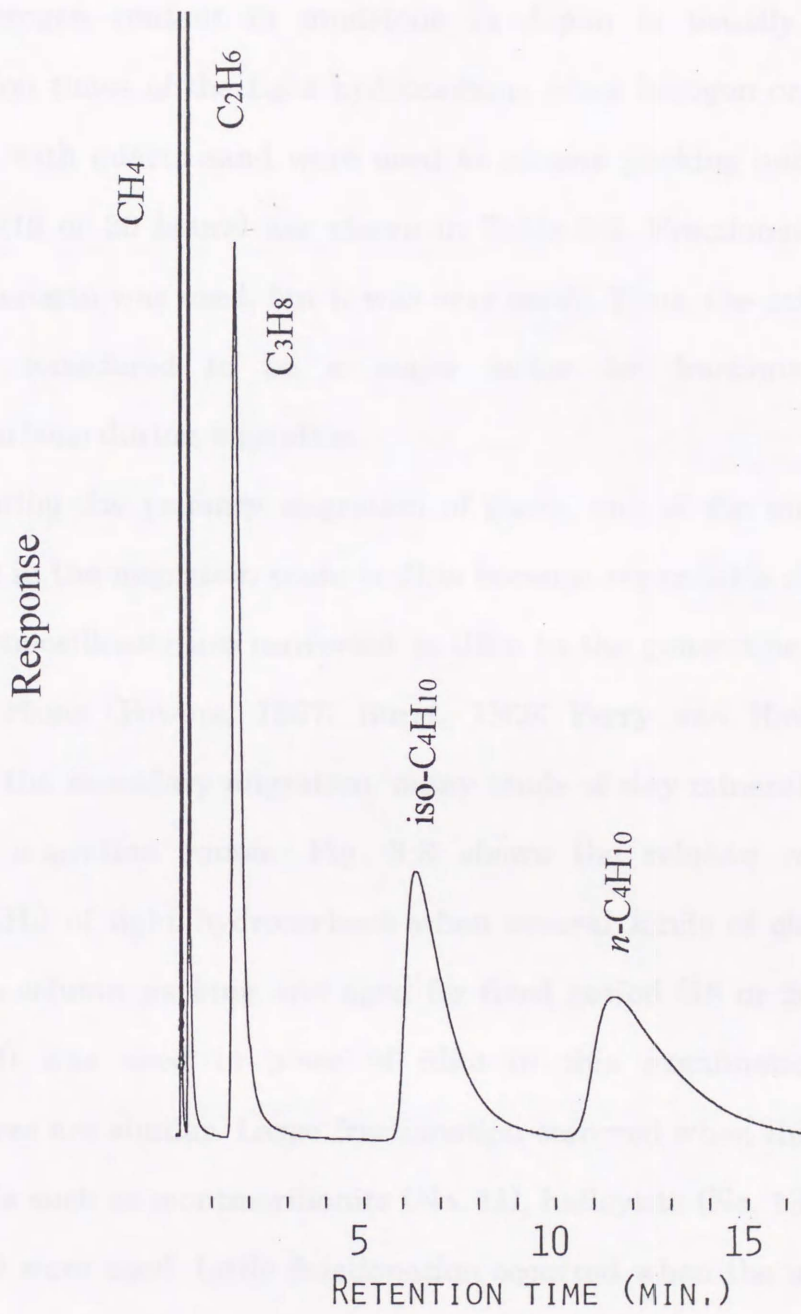


Fig. 3-2 Gas chromatogram of light hydrocarbons using a column packed with mudstone (No. 1) aged for 20 hours

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 mudstone in Japan is usually less than 2 %. Retention times of the light hydrocarbons when kerogen or coal (Nos. 19-21) diluted with quartz sand were used as column packing and aged for a fixed period (18 or 20 hours) are shown in Table 3-2. 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 montmorillonite 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. Fig. 3-3 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 examination 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 large fractionation when they have expandable interlayer spaces.

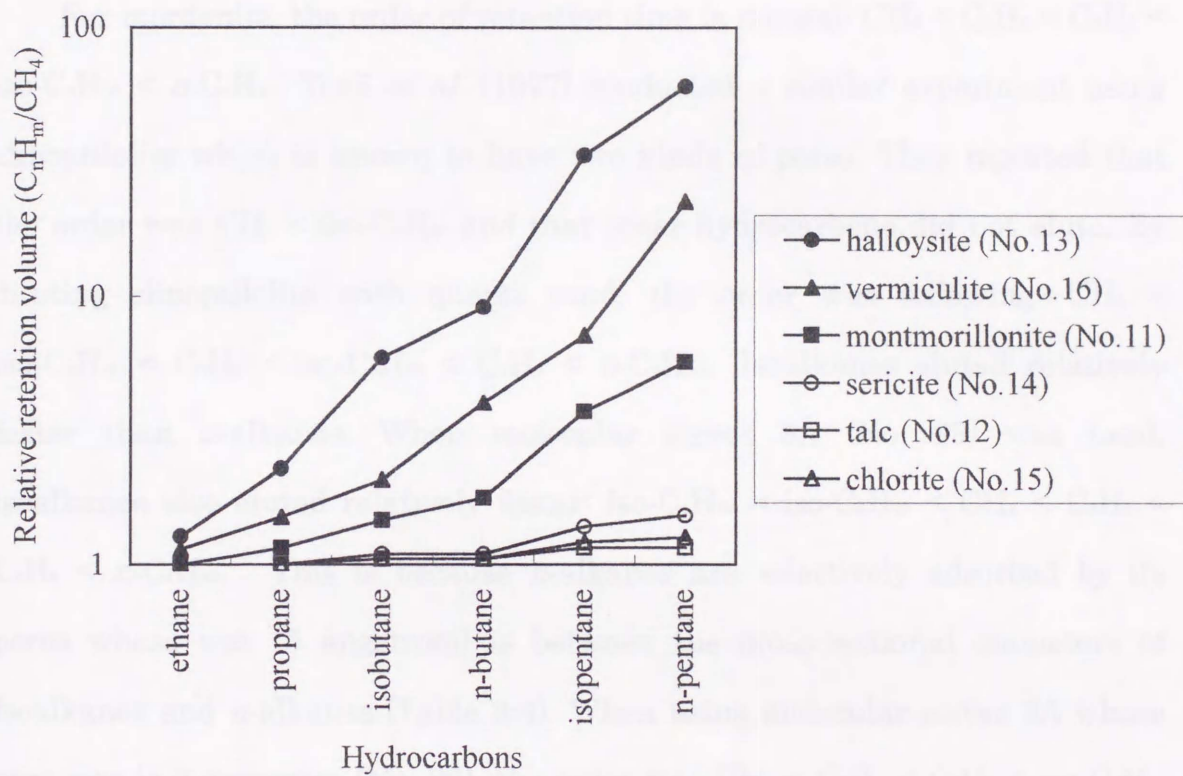


Fig. 3-3 Relative retention volumes ( $C_nH_m/CH_4$ ) of light hydrocarbons using columns packed with clay minerals

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 are shown in Fig. 3-4. 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:  $\text{CH}_4 < \text{C}_2\text{H}_6 < \text{C}_3\text{H}_8 < \text{iso-C}_4\text{H}_{10} < n\text{-C}_4\text{H}_{10}$ . Torii *et al.* (1977) conducted a similar experiment using clinoptilolite which is known to have two kinds of pores. They reported that the order was  $\text{CH}_4 < \text{iso-C}_4\text{H}_{10}$  and that other hydrocarbons did not elute. By diluting clinoptilolite with quartz sand, the order was following:  $\text{CH}_4 < \text{iso-C}_4\text{H}_{10} < \text{C}_2\text{H}_6 < \text{iso-C}_5\text{H}_{12} < \text{C}_3\text{H}_8 < n\text{-C}_4\text{H}_{10}$ . Isoalkanes eluted relatively faster than *n*-alkanes. When molecular sieves 5A (No. 23) was used, isoalkanes also eluted relatively faster:  $\text{iso-C}_4\text{H}_{10} = \text{iso-C}_5\text{H}_{12} < \text{CH}_4 < \text{C}_2\text{H}_6 < \text{C}_3\text{H}_8 < n\text{-C}_4\text{H}_{10}$ . This is because *n*-alkanes are selectively adsorbed by its pores whose size (5 angstrom) is between the cross-sectional diameters of isoalkanes and *n*-alkanes (Table 3-4). When using molecular sieves 3A whose pore size is 3 angstrom (No. 22), the order was  $\text{CH}_4 < \text{C}_2\text{H}_6 < \text{C}_3\text{H}_8 < \text{iso-C}_4\text{H}_{10} < n\text{-C}_4\text{H}_{10} < \text{iso-C}_5\text{H}_{12} < n\text{-C}_5\text{H}_{12}$ . When using mixture of molecular sieves 3A, 5A and quartz sand (No. 24), the order was  $\text{CH}_4 < \text{iso-C}_4\text{H}_{10} < \text{C}_2\text{H}_6 < \text{iso-C}_5\text{H}_{12} < \text{C}_3\text{H}_8 < n\text{-C}_4\text{H}_{10}$  (Fig. 3-5). 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 5A, while the other pore causes normal fractionation because the diameters of all the alkanes are larger than 3A.

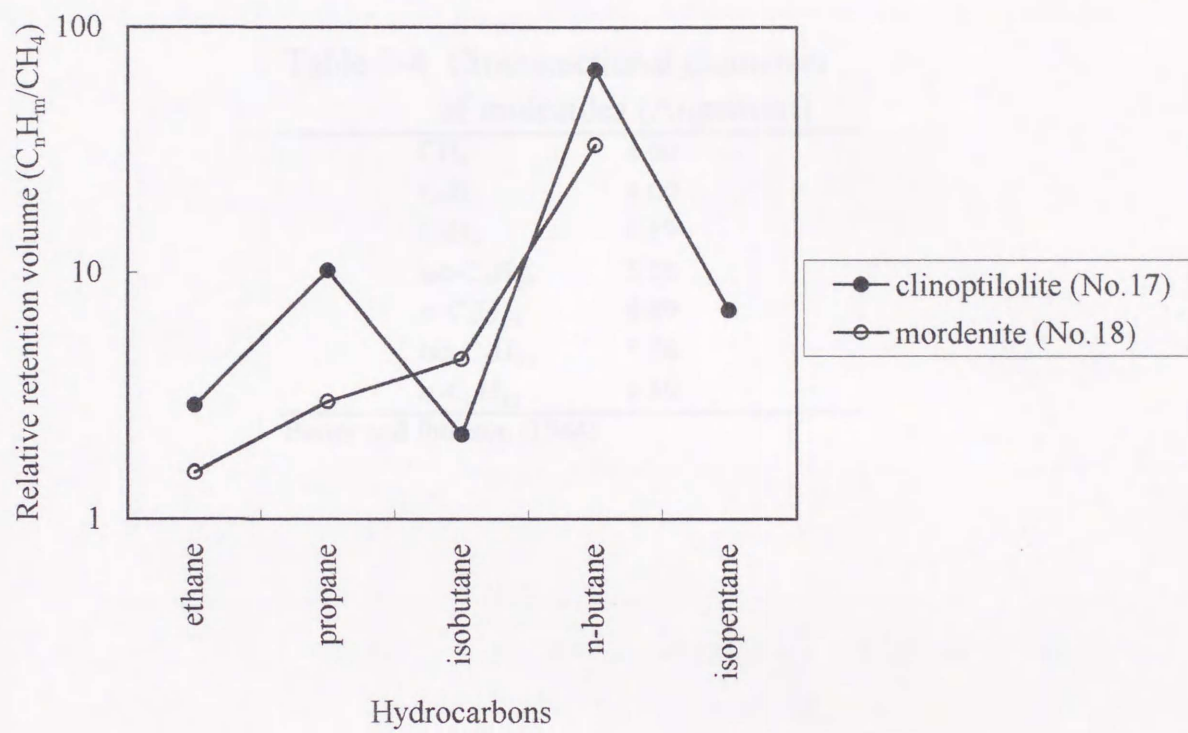


Fig. 3-4 Relative retention volumes ( $C_nH_m/CH_4$ ) of light hydrocarbons using columns packed with zeolites

Table 3-4 Cross-sectional diameters  
of molecules (Angstrom)

|  |      |
|--|------|
| CH <sub>4</sub>                          | 4.00 |
| C <sub>2</sub> H <sub>6</sub>            | 4.00 |
| C <sub>3</sub> H <sub>8</sub>            | 4.89 |
| iso-C <sub>4</sub> H <sub>10</sub>       | 5.58 |
| <i>n</i> -C <sub>4</sub> H <sub>10</sub> | 4.89 |
| iso-C <sub>5</sub> H <sub>12</sub>       | 5.58 |
| <i>n</i> -C <sub>5</sub> H <sub>12</sub> | 4.89 |

Barrer and Ibbitson (1944)

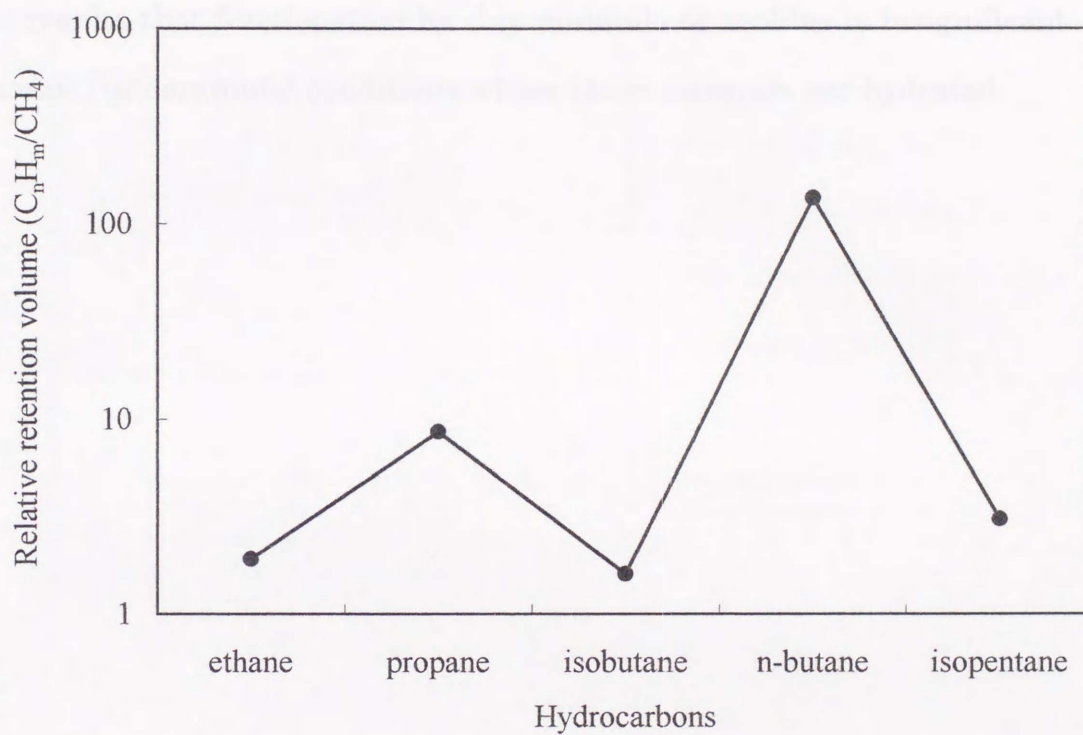


Fig. 3-5 Relative retention volumes ( $C_nH_m/CH_4$ ) of light hydrocarbons using columns packed with MS5A/MS3A/Qz sand (1/2/50)



The relative retention volumes ( $n\text{-C}_5\text{H}_{12}/\text{CH}_4$ ) using clay minerals and zeolites that were aged for various periods (0 to 20 h) are shown in Fig. 3-6 and Fig. 3-7 respectively. For expandable clay minerals and zeolites, the fractionation became larger with an 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 underground conditions where these minerals are hydrated.



Fig. 3-6 Relative retention volume  $n\text{-C}_5\text{H}_{12}/\text{CH}_4$  with various aging periods of ag. column packed with clay minerals.

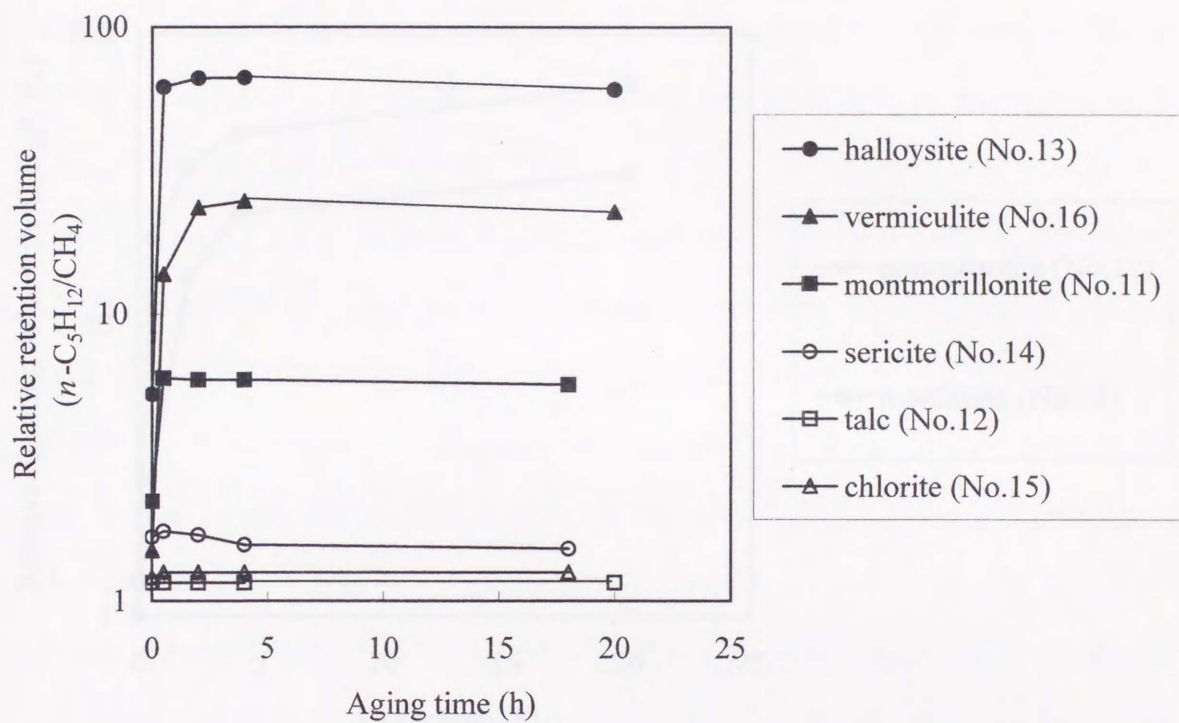


Fig. 3-6 Relative retention volumes ( $n\text{-C}_5\text{H}_{12}/\text{CH}_4$ ) with various aging periods using columns packed with clay minerals

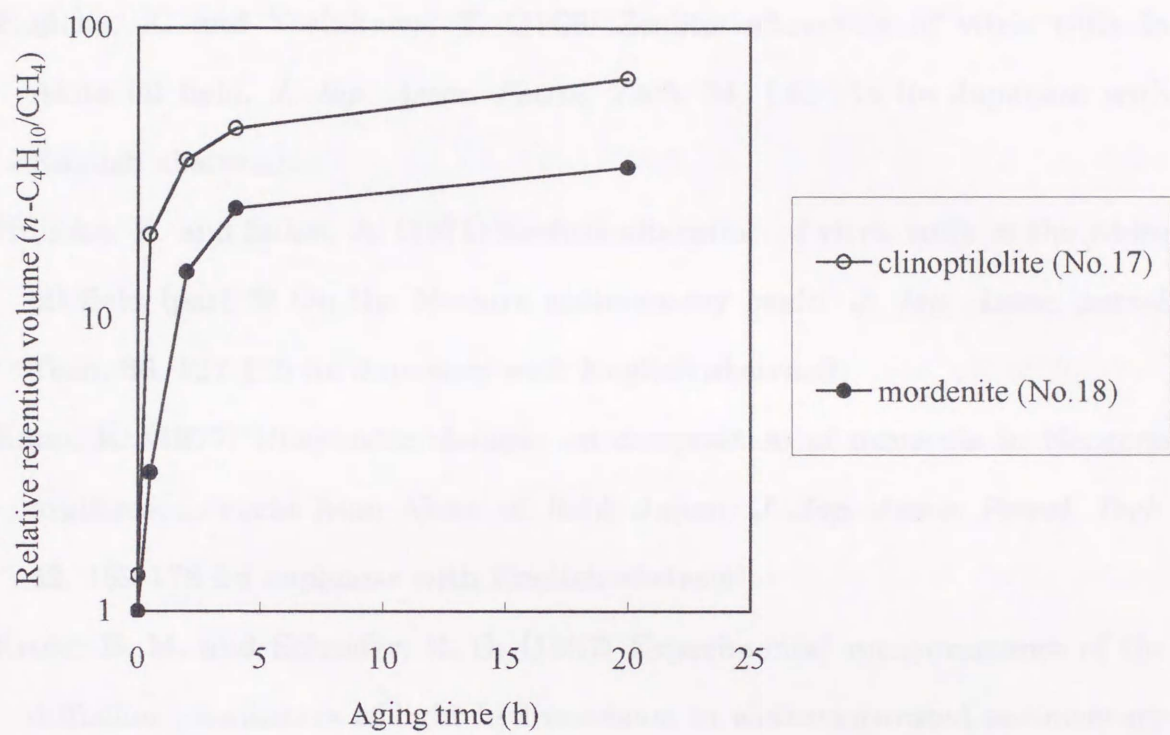


Fig. 3-7 Relative retention volumes ( $n\text{-C}_4\text{H}_{10}/\text{CH}_4$ ) with various aging periods using columns packed with zeolites

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## Chapter 4

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

6-1 Carbon isotopic ratios of methane in dissolved-in-water type gases: Origins of dissolved-in-water type gases.

## Chapter 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.

##### Summary

Carbon isotopic ratios of methane ( $\delta^{13}\text{C}(\text{CH}_4)$ ) were measured for dissolved-in-water type natural gases from several gas fields in Japan. Some samples have relatively low  $\delta^{13}\text{C}(\text{CH}_4)$  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  $\delta^{13}\text{C}(\text{CH}_4)$  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.



## Introduction

Natural gas of dissolved-in-water type is widely found in Japan. Many geological studies have been done to clear the formation processes of this type of gas deposits (e.g. Ijima, 1959; Sugisaki, 1964; Marsden and Kawai, 1965). However, there are few reports on the origin of dissolved-in-water type gas. Natural gases are divided into two types by their origin: biogenic and thermogenic gases (Schoell, 1983). Biogenic gas is produced by bacterial reduction of CO<sub>2</sub>, or bacterial decomposition of organic matter in formation water (Rice and Claypool, 1981). On the other hand, thermogenic gas is produced by thermal decomposition of kerogen in sediments. Nakai (1960) and Nakai *et al.* (1972) measured carbon and hydrogen isotopic compositions of dissolved-in-water type gases from the Niigata, Mobarra, 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 Kusakata gas field in Akita, and concluded that they are of biogenic origin with a small mixing of thermogenic gases. The present study extended chemical and carbon isotopic analyses to other gas fields, and tried to clarify the origins of the dissolved-in-water type gases in Japan.

## 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). They are listed in Table 2-1. Gas samples were collected by the water-displacement method at each gas well (Fig. 2-3). The samples were immediately introduced into Pyrex glass bottles at the sampling sites and the bottles were opened just before analysis in the laboratory.

### *Analysis*

Methane in each sample was separated with a Shimadzu 4CPF gas chromatograph (TCD detector) and introduced into a CuO combustion tube kept at 900 °C. The produced CO<sub>2</sub> and H<sub>2</sub>O were separated at the temperature of dry ice-ethanol mixture. The carbon isotopic ratio of CO<sub>2</sub> was measured with a Varian MAT 250 mass spectrometer (Fig. 4-1-1).

### **Results**

The carbon isotopic compositions of methane in the samples are listed in Table 4-1-1 (No. 1 for the gas field 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,  $\delta^{13}\text{C}(\text{CH}_4)$  value was -45.3 ‰. For the samples from Chiba, the range of  $\delta^{13}\text{C}(\text{CH}_4)$  values were -67.8 ~ -66.5 ‰. For the samples from Shizuoka, the range, of  $\delta^{13}\text{C}(\text{CH}_4)$  values were -46.8 ~ -33.8 ‰. For the samples from Miyazaki, the range of  $\delta^{13}\text{C}(\text{CH}_4)$  values were

Separation of each hydrocarbon by gas chromatograph  
(Packed column packed with silica gel)



Oxidation to CO<sub>2</sub> by CO<sub>2</sub> at 850°C



Measurement of CO<sub>2</sub> ratio m/z = 44, 45 and 46  
by mass spectrometer



Calculation of <sup>13</sup>C/<sup>12</sup>C



Calculation of δ<sup>13</sup>C

Fig.4-1-1 Analytical method of carbon isotopic ratios (<sup>13</sup>C/<sup>12</sup>C)

Table 4-1-1 Dissolved-in-water type gases  
and their carbon isotopic ratios

| No. | Area      | Gas field or<br>gas sign | $\delta^{13}\text{C}(\text{CH}_4)$<br>(‰) |
|-----|-----------|--------------------------|---|
| 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                                     |

-67.2 ~ -59.8 ‰. For the samples from Kagoshima, the range of  $\delta^{13}\text{C}(\text{CH}_4)$  values were -26.8 ~ -24.2 ‰.

## Discussion

Biogenic gases show low  $\delta^{13}\text{C}(\text{CH}_4)$  values (about -60 ~ -80 ‰) and contain small amounts of nonmethane hydrocarbons (Rice and Claypool, 1981). On the other hand, thermogenic gases show high  $\delta^{13}\text{C}(\text{CH}_4)$  values (about -25 ~ -45 ‰) and contain larger amounts of saturated nonmethane hydrocarbons. The latter is often associated with crude oil. Thermogenic gases sometimes lose nonmethane hydrocarbons during migration without significant changes in  $\delta^{13}\text{C}(\text{CH}_4)$  values (Sackett *et al.*, 1966; Schoell, 1983).

The estimated origins of the samples are listed in Table 4-1-2. 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  $\delta^{13}\text{C}(\text{CH}_4)$  values (-67.8 ~ -66.4 ‰). Natural gases of this type correspond to 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  $\delta^{13}\text{C}(\text{CH}_4)$  values (-46.8 ~ -24.2 ‰).

Table 4-1-2 Origins of dissolved-in-water type gases

| No. | Area             | Gas field or<br>gas sign | $\delta^{13}\text{C}(\text{CH}_4)$<br>/‰ | Origin      |
|-----|------------------|--------------------------|--|-------------|
| 1   | <i>Fukushima</i> | Nakoso                   | -45.3                                    | Mixed       |
| 3   | <i>Chiba</i>     | Narashino                | -67.8                                    | Biogenic    |
| 4   | <i>Chiba</i>     | Mobara-1                 | -67.0                                    | Biogenic    |
| 5   | <i>Chiba</i>     | Mobara-2                 | -67.1                                    | Biogenic    |
| 6   | <i>Chiba</i>     | Mobara-3                 | -66.5                                    | Biogenic    |
| 7   | <i>Chiba</i>     | Mobara-4                 | -66.9                                    | Biogenic    |
| 8   | <i>Chiba</i>     | Mobara-5                 | -67.0                                    | Biogenic    |
| 9   | <i>Chiba</i>     | Mobara-6                 | -67.0                                    | Biogenic    |
| 10  | <i>Chiba</i>     | Mobara-7                 | -67.3                                    | Biogenic    |
| 11  | <i>Shizuoka</i>  | Yaizu-1                  | -33.8                                    | Thermogenic |
| 12  | <i>Shizuoka</i>  | Yaizu-2                  | -34.2                                    | Thermogenic |
| 13  | <i>Shizuoka</i>  | Yaizu-3                  | -34.3                                    | Thermogenic |
| 14  | <i>Shizuoka</i>  | Shimizu                  | -46.8                                    | Mixed       |
| 15  | <i>Shizuoka</i>  | Fujieda-1                | -43.4                                    | Thermogenic |
| 16  | <i>Shizuoka</i>  | Fujieda-2                | -43.5                                    | Thermogenic |
| 17  | <i>Shizuoka</i>  | Haibara                  | -38.0                                    | Thermogenic |
| 18  | <i>Miyazaki</i>  | Sadohara-1               | -67.2                                    | Biogenic    |
| 19  | <i>Miyazaki</i>  | Sadohara-2               | -59.8                                    | Mixed       |
| 20  | <i>Miyazaki</i>  | Sadohara-3               | -66.4                                    | Biogenic    |
| 21  | <i>Kagoshima</i> | Shikine-1                | -24.2                                    | Thermogenic |
| 22  | <i>Kagoshima</i> | Shikine-2                | -26.8                                    | Thermogenic |

The sample from the Sadohara gas field (No. 19) is interpreted as a mixture of biogenic and thermogenic gases because of the intermediate  $\delta^{13}\text{C}(\text{CH}_4)$  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.

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## 4-2. Carbon isotopic ratios of methane, ethane and propane in oil field gases: Factors affecting the isotopic ratios.

### Summary

Carbon isotopic ratios of methane, ethane and propane ( $\delta^{13}\text{C}(\text{CH}_4)$ ,  $\delta^{13}\text{C}(\text{C}_2\text{H}_6)$  and  $\delta^{13}\text{C}(\text{C}_3\text{H}_8)$ , respectively) were analyzed for oil field gases from Niigata and Akita in Japan.

A strong correlation between  $\delta^{13}\text{C}(\text{C}_2\text{H}_6)$  and  $\delta^{13}\text{C}(\text{C}_3\text{H}_8)$  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  $\delta^{13}\text{C}(\text{CH}_4)$  and  $\delta^{13}\text{C}(\text{C}_2\text{H}_6)$ . The weak correlation is inferred to be due to a mixing of biogenic gas that has low  $\delta^{13}\text{C}(\text{CH}_4)$ . Furthermore, mixing ratios of thermogenic gas and biogenic gas can be calculated from  $\delta^{13}\text{C}(\text{CH}_4)$ ,  $\delta^{13}\text{C}(\text{C}_2\text{H}_6)$  and  $\delta^{13}\text{C}(\text{C}_3\text{H}_8)$ . It is found that almost all the oil field gases in Akita and Niigata are mixture of thermogenic and biogenic gases.

## Introduction

Thermogenic gases show high  $\delta^{13}\text{C}(\text{CH}_4)$  (about  $-25 \sim -45 \text{ ‰}$ ) (Shoell, 1983). On the other hand, biogenic gases show low  $\delta^{13}\text{C}(\text{CH}_4)$  (about  $-60 \sim -70 \text{ ‰}$ ) (Rice and Claypool, 1981). Furthermore,  $\delta^{13}\text{C}(\text{CH}_4)$  is used to estimate the maturity of thermogenic gas (Schoell, 1983). Several studies have been carried out to examine the origin of oil field gases from Niigata and Akita in Japan by using  $\delta^{13}\text{C}(\text{CH}_4)$  (Waseda and Omokawa, 1988; Sakata *et al.*, 1989). However,  $\delta^{13}\text{C}(\text{CH}_4)$  of thermogenic gases changes by mixing with biogenic gases. Therefore  $\delta^{13}\text{C}(\text{C}_2\text{H}_6)$ ,  $\delta^{13}\text{C}(\text{C}_3\text{H}_8)$  and  $\delta^{13}\text{C}(\text{CH}_4)$  were measured for oil field gases in Niigata and Akita, because they are not affected by the mixing of biogenic gas. Furthermore, factors determining those values of oil field gases in Akita and Niigata are clarified.

## Experiments

### *Samples*

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). Gas samples from gas wells were collected by the water-displacement method (Fig. 2-3). The samples were immediately stored in Pyrex glass bottles at the sampling sites, and the bottles were opened just before analysis in laboratory.

### Analysis

Methane, ethane and propane in each sample were separated with a Shimadzu 4CPF gas chromatograph (TCD detector) and introduced into a CuO combustion tube kept at 900 °C. The produced CO<sub>2</sub> and H<sub>2</sub>O were separated at the temperature of dry ice-ethanol mixture. The carbon isotopic ratio of CO<sub>2</sub> was measured with a Varian MAT 250 mass spectrometer.

### Results

For the samples from Niigata,  $\delta^{13}\text{C}(\text{CH}_4)$ ,  $\delta^{13}\text{C}(\text{C}_2\text{H}_6)$  and  $\delta^{13}\text{C}(\text{C}_3\text{H}_8)$  were in the range of -43.8 ‰ ~ -33.1 ‰, -25.5 ‰ ~ -23.2 ‰ and -22.8 ‰ ~ -21.9 ‰, respectively as shown in Table 4-2-1 (Nos. 38 - 51). For the Akita samples,  $\delta^{13}\text{C}(\text{CH}_4)$ ,  $\delta^{13}\text{C}(\text{C}_2\text{H}_6)$  and  $\delta^{13}\text{C}(\text{C}_3\text{H}_8)$  were in the range of -56.4 ‰ ~ -36.4 ‰, -33.0 ‰ ~ -25.6 ‰ and -28.1 ‰ ~ -23.1 ‰, respectively as shown in Table 4-2-1 (Nos. 23-37).

### 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  $\delta^{13}\text{C}(\text{CH}_4)$  values (-56.4 ‰ ~ -33.1 ‰). This result does not conflict with the results of Sakata *et al.* (1986), and Waseda and Omokawa (1988).

The  $\delta^{13}\text{C}(\text{C}_2\text{H}_6)$  vs.  $\delta^{13}\text{C}(\text{C}_3\text{H}_8)$  diagram is shown in Fig. 4-2-1. There is a

Table 4-2-1 Oil field gases and their carbon isotopic ratios of methane, ethane and propane

| No. Location        | $\delta^{13}\text{C}(\text{CH}_4)$<br>/‰ | $\delta^{13}\text{C}(\text{C}_2\text{H}_6)$<br>/‰ | $\delta^{13}\text{C}(\text{C}_3\text{H}_8)$<br>/‰ |
|---------------------|--|---|---|
| <i>Akita</i>        |  |   |   |
| 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       | -36.4                                    | -25.6   | -23.8   |
| 37 Yurihara-2       | -52.1                                    | -27.0   | -24.7   |
| <i>Niigata</i>      |  |   |   |
| 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

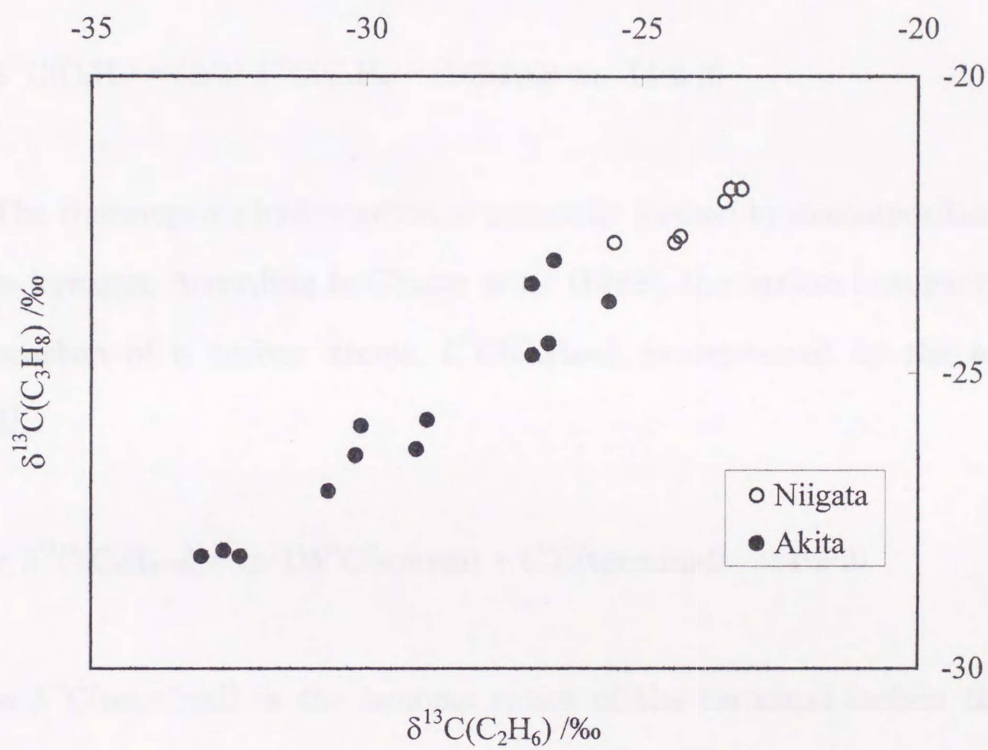


Fig. 4-2-1 Relation between  $\delta^{13}\text{C}(\text{C}_2\text{H}_6)$  and  $\delta^{13}\text{C}(\text{C}_3\text{H}_8)$

strong correlation ( $r = 0.98$ ) between these two values. By the method of least squares, the correlation is shown as Eq. (4-2-1).

$$\delta^{13}\text{C}(\text{C}_3\text{H}_8) = 0.662 \delta^{13}\text{C}(\text{C}_2\text{H}_6) - 6.44 \text{‰} \quad (4-2-1)$$

After approximation in Eq. (4-2-1)

$$\delta^{13}\text{C}(\text{C}_3\text{H}_8) = (2/3) \delta^{13}\text{C}(\text{C}_2\text{H}_6) - (1/3)19.3 \text{‰} \quad (4-2-2)$$

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,  $\delta^{13}\text{C}(\text{C}_n\text{H}_{2n+2})$ , is expressed by the equation (4-2-3),

$$n \delta^{13}\text{C}(\text{C}_n\text{H}_{2n+2}) = (n-1)\delta^{13}\text{C}(\text{source}) + \delta^{13}\text{C}(\text{terminal}) \quad (4-2-3)$$

where  $\delta^{13}\text{C}(\text{terminal})$  is the isotopic ratios of the terminal carbon that was originally bound to the source kerogen, and  $\delta^{13}\text{C}(\text{source})$  is the carbon isotopic ratios of the source kerogen. Chung *et al.* (1988) assumed that  $\delta^{13}\text{C}(\text{terminal})$  is smaller than  $\delta^{13}\text{C}(\text{source})$  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  $\delta^{13}\text{C}(\text{source})$  are not affected by the kinetic isotope effect.

Equation (4-2-3) indicates that  $\delta^{13}\text{C}(\text{C}_n\text{H}_{2n+2})$  is expressed as the weighted

average of (n-1) carbon atoms of the same isotopic ratios as the source kerogen and terminal carbon of  $\delta^{13}\text{C}(\text{terminal})$ .

After rearrangement, and substituting 2 or 3 for n, the isotopic ratios for thermogenic ethane  $\delta^{13}\text{C}(\text{C}_2\text{H}_6)$  and propane  $\delta^{13}\text{C}(\text{C}_3\text{H}_8)$  are expressed as follows:

$$\delta^{13}\text{C}(\text{C}_2\text{H}_6) = (1/2)\delta^{13}\text{C}(\text{source}) + (1/2)\delta^{13}\text{C}(\text{terminal}) \quad (4-2-4)$$

$$\delta^{13}\text{C}(\text{C}_3\text{H}_8) = (2/3)\delta^{13}\text{C}(\text{source}) + (1/3)\delta^{13}\text{C}(\text{terminal}) \quad (4-2-5)$$

Assuming that an ethane-propane pair in a sample came from the same source kerogen and has the same  $\delta^{13}\text{C}(\text{terminal})$  (Chung *et al.*, 1988), the relation between  $\delta^{13}\text{C}(\text{C}_2\text{H}_6)$  and  $\delta^{13}\text{C}(\text{C}_3\text{H}_8)$  is expressed as follows:

$$\delta^{13}\text{C}(\text{C}_3\text{H}_8) = (2/3)\delta^{13}\text{C}(\text{C}_2\text{H}_6) + (1/3)\delta^{13}\text{C}(\text{source}) \quad (4-2-6)$$

Eq. (4-2-2) shows accordance with Eq. (4-2-6). This shows that changes of  $\delta^{13}\text{C}(\text{C}_2\text{H}_6)$  and  $\delta^{13}\text{C}(\text{C}_3\text{H}_8)$  of oil field gases from Akita and Niigata were controlled kinetically and  $\delta^{13}\text{C}(\text{source})$  of the gases are close to each other (about -19.3 ‰).

The  $\delta^{13}\text{C}$  of oil produced from oil and gas fields is shown in Table 4-2-2. It is known that  $\delta^{13}\text{C}$  of kerogen and coexisting bitumen strongly correlate to each other (Shimoyama and Matsubaya, 1985), and that the difference between  $\delta^{13}\text{C}$  of oil and source kerogen is only 0.5 ~ 3 ‰ (Omokawa, 1985). If fractionation between oil and source kerogen is 3 ‰,  $\delta^{13}\text{C}$  of source kerogen



Table 4-2-2 Carbon isotopic ratios of oils

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

ND: no data

\*Omokawa(1985)

\*\*Okada *et al.* (1989)

\*\*\*Waseda and Omokawa (1990)

in the studied area is inferred to be about  $-19.0 \sim -20.8$  ‰. This value does not conflict with the calculated source kerogen value ( $-19.3$  ‰).

For the cleavage reaction of  $^{12}\text{C}$ -source bond, rate constant  $k_{12}$  is expressed by Eq. (4-2-7),

$$k_{12} = A_{12} \exp(-E_{12}/RT) \quad (4-2-7)$$

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  $^{13}\text{C}$ -source bond, rate constant  $k_{13}$  is expressed by eq. (4-2-8).

$$k_{13} = A_{13} \exp(-E_{13}/RT) \quad (4-2-8)$$

After rearrangement,

$$k_{13}/k_{12} = (A_{13}/A_{12})\exp((E_{12} - E_{13})/RT) \quad (4-2-9)$$

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

Calculated  $\delta^{13}\text{C}(\text{terminal}) - \delta^{13}\text{C}(\text{source})$  of the samples are shown in Table 4-2-3. The values of the samples from Niigata are much smaller than those from Akita. This shows samples from Niigata were generated at a higher temperature than those from Akita. Reservoir temperatures are shown in

Table 4-2-3 Calculated  $\delta^{13}\text{C}(\text{terminal}) - \delta^{13}\text{C}(\text{source})$

| No. Location        | Calculated<br>$\delta^{13}\text{C}(\text{terminal}) - \delta^{13}\text{C}(\text{source})$<br>/‰ |
|---------------------|---|
| 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 4-2-4. The average of the median temperatures of the reservoirs from Niigata (89 °C) is higher than that from Akita (64 °C). It is inferred from this fact that the generation temperature 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  $\delta^{13}\text{C}(\text{CH}_4)$  and  $\delta^{13}\text{C}(\text{C}_2\text{H}_6)$  as shown in Fig. 4-2-2. Substituting  $n = 1$  or  $2$  in Eq. (4-2-6) and after rearrangement,

$$\delta^{13}\text{C}(\text{C}_2\text{H}_6) = (1/2)\delta^{13}\text{C}(\text{CH}_4) + (1/2)\delta^{13}\text{C}(\text{source}) \quad (4-2-10)$$

The calculated line, when  $-19.3$  ‰ is used for  $\delta^{13}\text{C}(\text{source})$  in Eq. (4-2-10), is also shown in Fig. 4-2-2. The measured  $\delta^{13}\text{C}(\text{CH}_4)$  was close to or lower than the calculated  $\delta^{13}\text{C}(\text{CH}_4)$ . This indicates the thermogenic gas mixed with biogenic gas that has low  $\delta^{13}\text{C}(\text{CH}_4)$  value (about  $-67$  ‰ in Japan (Nakai *et al.*, 1974)) and little nonmethane hydrocarbons.

The mixing ratios (methane) of thermogenic gas and biogenic gas can be calculated as follows when the  $\delta^{13}\text{C}(\text{CH}_4)$  value of biogenic gas is  $-67$  ‰.

Substituting 1 for  $n$  in Eq. (4-2-3)

$$\delta^{13}\text{C}(\text{CH}_4)_{\text{calc}} = \delta^{13}\text{C}(\text{terminal}) \quad (4-2-11)$$

By rearrangement of Eq. (4-2-3) and (4-2-4)

Table 4-2-4 Reservoir temperatures

| Location       | Reservoir temperature<br>°C | Median temperature<br>°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)

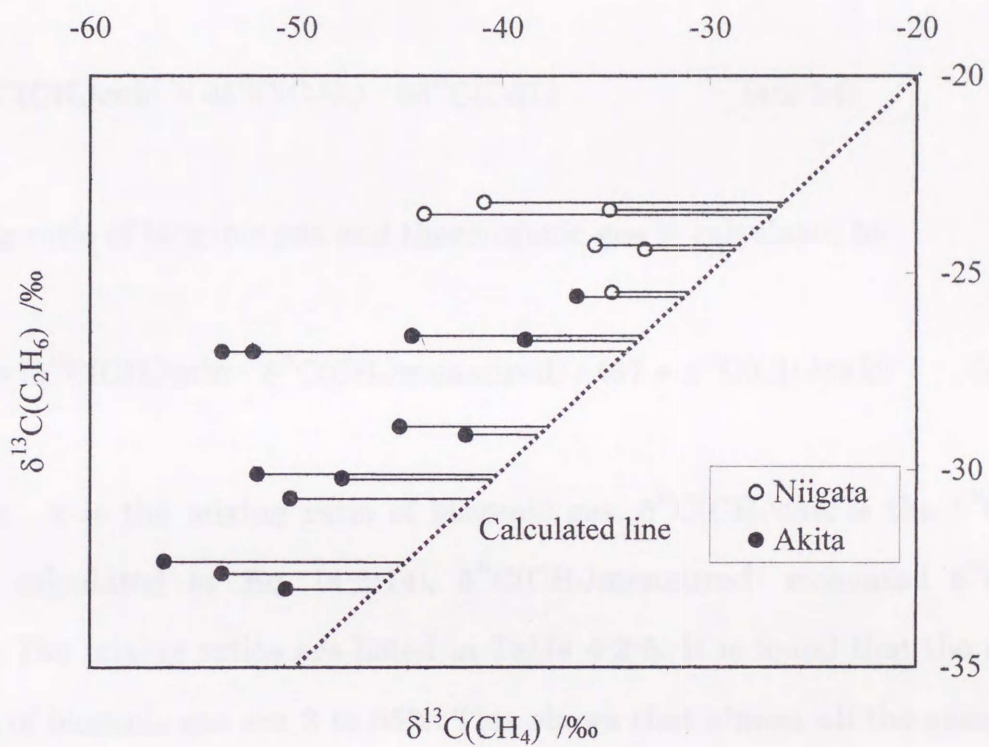


Fig. 4-2-2 Relation between  $\delta^{13}\text{C}(\text{CH}_4)$  and  $\delta^{13}\text{C}(\text{C}_2\text{H}_6)$

$$\delta^{13}\text{C}(\text{C}_2\text{H}_6) = (1/2)\delta^{13}\text{C}(\text{source}) + (1/2)\delta^{13}\text{C}(\text{CH}_4)\text{calc} \quad (4\cdot2\cdot12)$$

$$\delta^{13}\text{C}(\text{C}_3\text{H}_8) = (2/3)\delta^{13}\text{C}(\text{source}) + (1/3)\delta^{13}\text{C}(\text{CH}_4)\text{calc} \quad (4\cdot2\cdot13)$$

After rearrangement of Eqs. (4-2-12) and (4-2-13),

$$\delta^{13}\text{C}(\text{CH}_4)\text{calc} = 4\delta^{13}\text{C}(\text{C}_3\text{H}_8) - 3\delta^{13}\text{C}(\text{C}_2\text{H}_6) \quad (4\cdot2\cdot14)$$

Mixing ratio of biogenic gas and thermogenic gas is calculated by

$$x = (\delta^{13}\text{C}(\text{CH}_4)\text{calc} - \delta^{13}\text{C}(\text{CH}_4)\text{measured}) / (67 + \delta^{13}\text{C}(\text{CH}_4)\text{calc}) \quad (4\cdot2\cdot15)$$

Where,  $x$  is the mixing ratio of biogenic gas,  $\delta^{13}\text{C}(\text{CH}_4)\text{calc}$  is the  $\delta^{13}\text{C}(\text{CH}_4)$  value calculated by Eq. (4-2-14),  $\delta^{13}\text{C}(\text{CH}_4)\text{measured}$ : measured  $\delta^{13}\text{C}(\text{CH}_4)$  value. The mixing ratios are listed in Table 4-2-5. It is found that the mixing ratios of biogenic gas are 3 to 55%. This shows that almost all the gases from Akita and Niigata are mixed with biogenic gas.

Table 4-2-5 Mixing ratios of biogenic gas and thermogenic gas (CH<sub>4</sub>)

|                      | $\delta^{13}\text{C}(\text{CH}_4)$<br>/‰ | thermogenic<br>/% | biogenic<br>/% |
|----------------------|--|-------------------|----------------|
| <i>Akita</i>         |  |                   |                |
| 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             |
| <i>Niigata</i>       |  |                   |                |
| 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              |



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Hydroxide compositions including nitrogen, which has been well known, of major natural gases in Nigeria are described. It is suggested that the composition of hydroxide composition is a major factor of the hydroxide composition of natural gas.

## Chapter 5.

The composition of hydroxide composition in Nigeria was investigated by a differential technique using a chromatograph. It was found that the composition change due to nitrogen is a major factor in the hydroxide composition.

## Summary and conclusions

The composition of hydroxide composition in Nigeria was investigated by a differential technique using a chromatograph. It was found that the composition change due to nitrogen is a major factor in the hydroxide composition. The composition of hydroxide composition in Nigeria was investigated by a differential technique using a chromatograph. It was found that the composition change due to nitrogen is a major factor in the hydroxide composition.

Hydrocarbon compositions including neopentane, which has been rarely measured, of major natural gases in Japan are examined. It is presumed 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 the compositional change due to migration under normal underground conditions is insignificant.

The  $\delta^{13}\text{C}(\text{CH}_4)$  values of dissolved-in-water type gases were measured. Using these values it was possible to find the origins of the gases; biogenic, thermogenic or mixed origin of both types.

The  $\delta^{13}\text{C}(\text{CH}_4)$ ,  $\delta^{13}\text{C}(\text{C}_2\text{H}_6)$  and  $\delta^{13}\text{C}(\text{C}_3\text{H}_8)$  values were measured for oil field gases in Niigata and Akita. It was found that almost all the samples are of mixed origin of thermogenic and biogenic gases. Furthermore, the mixing ratios of both type gases could be estimated using the isotopic values.

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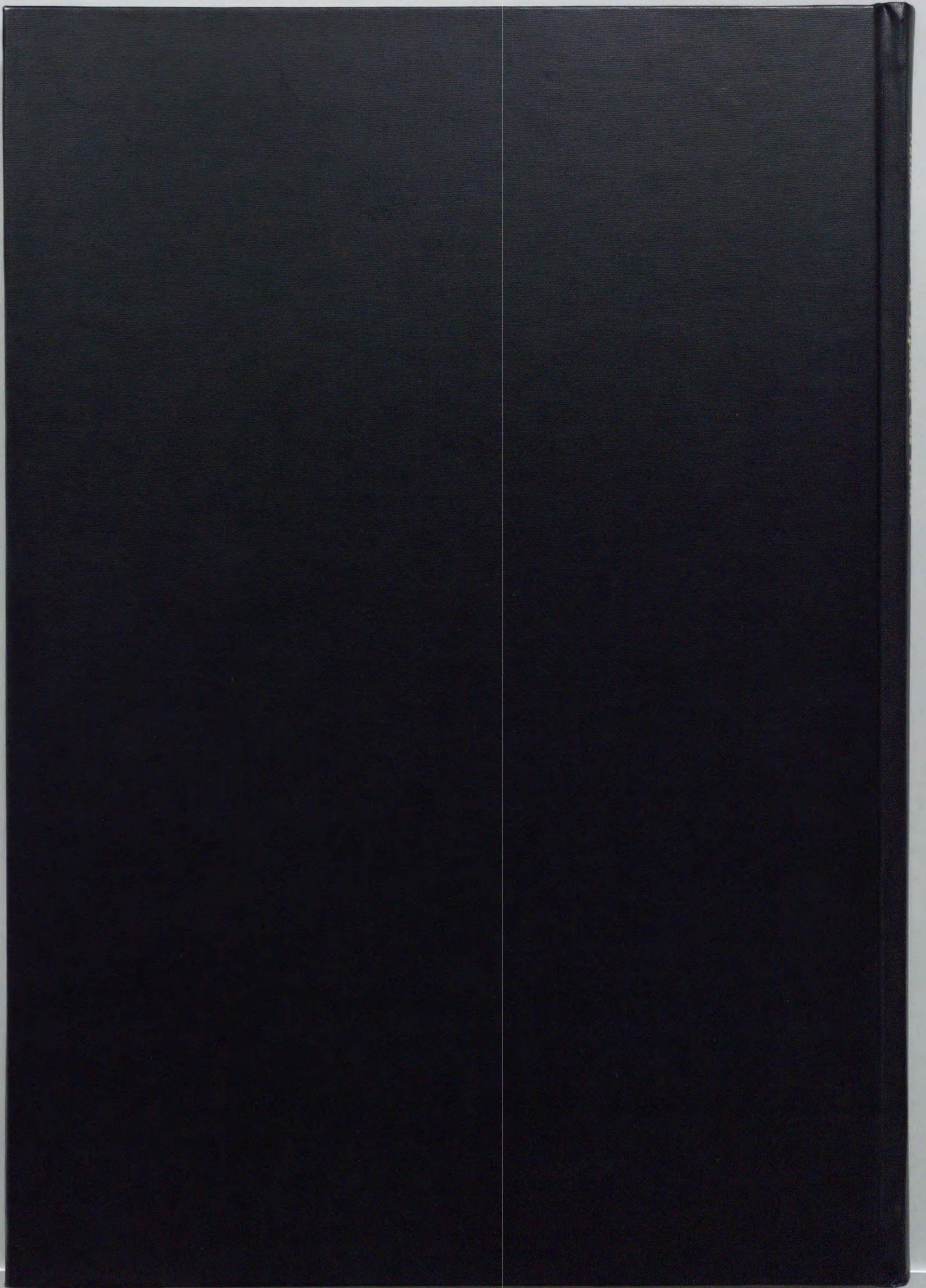
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January, 2001

Shunichiro IGARI





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Yellow

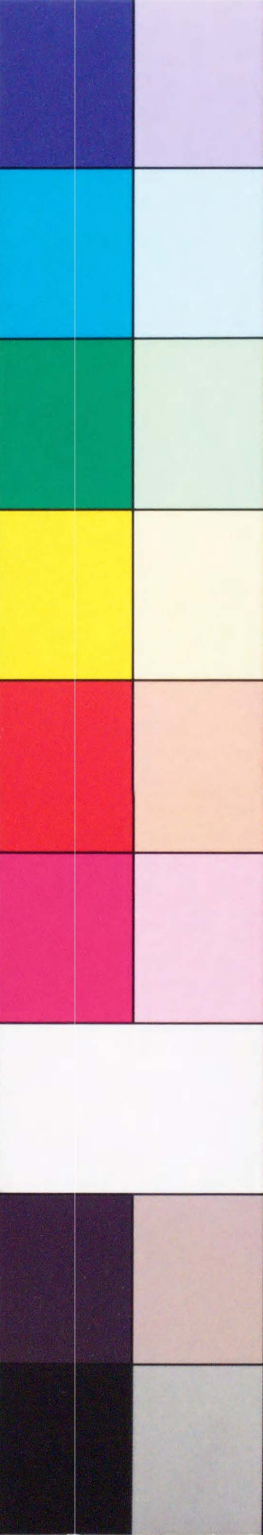
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