Geochemical Journal, Vol. 41, pp. 57 to 63, 2007

Pentane and hexane isomers in natural gases from oil and gas fields in Akita, Niigata and Hokkaido, Japan: Determination factor in their isomer ratios

SHUN-ICHIRO IGARI* TATSUO MAEKAWA and YUICHIRO SUZUKI

National Institute of Advanced Industrial Science and Technology, Tsukuba 305-8567, Japan

(*Received December 8, 2005; Accepted October 13, 2006*)

Hydrocarbons are the main components in natural gases. Although the molecular distribution has been often used to study the origin of hydrocarbon, the occurrence of pentane and hexane isomers has not been discussed for natural gases. This study first reports controlling factors of pentane and hexane isomer ratios of natural gases from Akita, Niigata and Hokkaido in Japan. For the samples from Akita and Niigata, pentane and hexane isomer ratios such as neopentane/isopentane and 2,2-dimethylbutane/2,3-dimethylbutane show positive correlations with $\delta^{13}C$ (ethane), suggesting that the ratios are affected by the generation temperature.

Relation between kerogen type and isobutane/*n*-butane ratio is also discussed. By the comparison between Akita and Niigata gases that originated from type II kerogen and Hokkaido gases that originated from type III kerogen, the gases from type III kerogen show a higher isobutane/*n*-butane ratio compared with those originated from type II kerogen.

Although carbon isotopic ratios of ethane and propane are good parameters for the gas generation temperature, this study indicates that combinations among pentane isomer ratios and hexane isomer ratios also provide good parameters for the gas generation temperature.

Keywords: pentane isomers, hexane isomers, natural gas, Japan

INTRODUCTION

The main components in natural gases are hydrocarbons. There have been several reports on the hydrocarbon composition of Japan's natural gases. Sakata *et al.* (1986), and Waseda and Omokawa (1988) measured hydrocarbon compositions of gases from the Akita and Niigata oil fields.

The main component in natural gas hydrocarbons is methane. The concentrations of non-methane hydrocarbons in natural gas depend on their origin. Thermogenic gas shows relatively high concentrations of non-methane hydrocarbons, and biogenic gas shows low concentrations (Schoell, 1983).

For thermogenic gas, the non-methane hydrocarbon composition depends on the maturity (Schoell, 1983) and type of kerogen (Rice, 1983). Connan and Cassou (1980) showed the isobutane/*n*-butane ratio depends on the maturity; immature condensates show a high isobutane/*n*-butane ratio. However, for high wax crude oils and mature condensates, the correlation between the isobutane/*n*-butane ratio and maturity is unclear. As for gases in Japan, Kato (1989) showed the isobutane/*n*-butane ratio correlates with maturity; more mature gas shows a high isobutane/*n*-butane ratio. For the kerogen type, gases from type III kerogen show a relatively low concentration of non-methane hydrocarbon (Chen *et al.*, 2000). As for gases in Japan, Yonetani (1986) showed the isobutane/*n*-butane ratio depends on the type of kerogen; gases from a terrestrial origin show a high isobutane/*n*-butane ratio, but the reason is unclear. Secondary processes such as bacterial degradation and migration also affect the non-methane hydrocarbon concentration. As for bacterial degradation, *n*-alkanes are selectively degraded by bacteria (James and Burns, 1984). Concerning migration, higher molecular weight hydrocarbons show lower diffusion coefficients (Whiticar, 1994).

Thus, factors affecting the hydrocarbon composition have been partly clarified. However, as mentioned above, the hydrocarbons are mainly discussed for methane, ethane, propane, isobutane and *n*-butane. There are only a few studies on pentane and hexane isomers. Igari (1996) reported on pentane isomers in natural gases in Japan, implying that hydrogen abstraction by a hydroxyl radical affects the hydrocarbon composition of dissolved-in-water type gases. In addition, Igari (2001) reported the occurrence of pentane and hexane isomers in natural gases from the Akita and Niigata oil fields. However, isomer ratios of pentane and hexane along with their controlling factors have never been clarified with respect to the for-

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*Corresponding author (e-mail: s-igari@aist.go.jp)

Table 1. Hydrocarbon composition and δ^{13}C(ethane) of natural gases from Niigata, Akita and Hokkaido, Japan

No.	Location	δ^{13}C(ethane) (‰)	methane (%)	ethane (%)	propane (%)	isobutane (%)	*n*-butane (%)	neopentane (%)	isopentane (%)	*n*-pentane (%)
Niigata										
39[c]	Mitsuke-2	−23.4[a]	84.6	5.85	2.15	0.42	0.52	0.0043	0.15	0.08
40[c]	Higashi-Niigata-1	−23.5[b]	87.4	4.51	1.89	0.41	0.53	0.0034	0.18	0.11
41[c]	Higashi-Niigata-2	−23.1[b]	84.6	6.21	2.44	0.54	0.72	0.0050	0.28	0.18
42[c]	Higashi-Niigata-3	−21.6[a]	78.2	4.79	1.63	0.40	0.46	0.0051	0.19	0.11
45[c]	Minami-Nagaoka	−22.0[b]	80.7	4.76	1.60	0.40	0.42	0.0041	0.16	0.09
46[c]	Katakai	−23.9[b]	80.6	5.48	1.93	0.37	0.48	0.0032	0.16	0.11
48[c]	Higashi-Kashiwazai	−24.1[b]	85.4	5.03	1.97	0.45	0.52	0.0052	0.19	0.12
49[c]	Kubiki-1	−26.0[b]	88.0	4.55	1.19	0.36	0.37	0.0033	0.17	0.09
Akita										
23[c]	Yabase-1	−27.0[a]	75.3	5.23	6.98	1.36	2.36	0.0059	0.50	0.27
24[c]	Yabase-2	−29.1[d]	72.1	9.20	5.99	0.96	2.25	0.0056	0.84	0.72
25[c]	Yabase-3	−26.7[d]	79.5	8.56	3.71	0.56	1.02	0.0034	0.30	0.24
29[c]	Sarukawa-1	−33.0[a]	62.6	9.01	12.40	1.91	3.30	0.0074	0.64	0.41
30[c]	Sarukawa-2	−32.5[b]	83.6	5.64	3.01	0.37	0.67	0.0016	0.22	0.14
31[c]	Sarukawa-3	−32.6[d]	63.7	8.01	7.30	1.09	2.24	0.0043	0.53	0.39
33[c]	Nishioogata-1	−30.1[b]	76.2	8.19	4.24	0.80	1.35	0.0058	0.64	0.39
36[c]	Yurihara-1	−25.6[a]	77.6	9.86	4.70	0.67	0.98	0.0036	0.20	0.15
Hokkaido										
52	Yufutsu-1	ND	83.7	7.53	2.86	0.75	0.63	0.0046	0.19	0.14
53	Yufutsu-2	ND	83.5	7.01	2.58	0.68	0.6	0.0046	0.19	0.15
54	Yufutsu-3	−25.3	83.4	7.19	2.59	0.68	0.59	0.0046	0.19	0.14

No.	Location	2.2DMB (%)	2.3DMB (%)	2MP (%)	3MP (%)	*n*-hexane (%)
Niigata						
39[d]	Mitsuke-2	0.0036	0.0069	0.012	0.007	0.006
40[d]	Higashi-Niigata-1	0.0039	0.010	0.024	0.014	0.015
41[d]	Higashi-Niigata-2	0.0070	0.020	0.041	0.024	0.030
42[d]	Higashi-Niigata-3	0.0056	0.0089	0.026	0.014	0.017
45[d]	Minami-Nagaoka	0.0047	0.0091	0.021	0.013	0.018
46[d]	Katakai	0.0042	0.011	0.024	0.015	0.021
48[d]	Higashi-Kashiwazai	0.0061	0.013	0.032	0.019	0.029
49[d]	Kubiki-1	0.0032	0.016	0.024	0.015	0.016
Akita						
23[d]	Yabase-1	0.0026	0.018	0.029	0.016	0.010
24[d]	Yabase-2	0.0084	0.123	0.176	0.117	0.135
25[d]	Yabase-3	0.0041	0.022	0.052	0.032	0.041
29[d]	Sarukawa-1	0.0031	0.025	0.042	0.025	0.023
30[d]	Sarukawa-2	0.0016	0.013	0.022	0.015	0.0078
31[d]	Sarukawa-3	0.0029	0.034	0.055	0.035	0.037
33[d]	Nishioogata-1	0.0085	0.033	0.063	0.037	0.022
36[d]	Yurihara-1	0.0023	0.012	0.024	0.013	0.021
Hokkaido						
52	Yufutsu-1	0.0042	0.011	0.034	0.016	0.039
53	Yufutsu-2	0.0048	0.014	0.043	0.019	0.049
54	Yufutsu-3	0.0055	0.013	0.037	0.018	0.047

[a] *Igari (1999a);* [b] *Sakata (1991);* [c] *Hydrocarbon composition data; Igari (1996);* [d] *Igari (2001).*
ND: no data.

mation mechanisms of natural gases. In the present study, the determination factor of pentane and hexane isomers in natural gases from Akita, Niigata and Hokkaido is discussed.

ANALYTICAL PROCEDURE

Concentrations of methane, ethane, propane, isobutane, *n*-butane, neopentane, isopentane, *n*-pentane, 2,2-dimethylbutane (2,2-DMB), 2,3-dimethylbutane (2,3-DMB), 2-methylpentane (2-MP), 3-methylpentane (3-MP) and *n*-hexane are determined by gas chromatography for the samples from the Yufutsu oil and gas field in Hokkaido, Japan (Table 1). The analytical conditions are shown elsewhere (Igari, 2001). Carbon isotopic composition of ethane (δ^{13}C(ethane)) for the sample from the Yufutsu oil and gas field is measured by the Japan Petroleum Exploration Co. The δ^{13}C(ethane) value is reported relative to Peedee Belemnite.

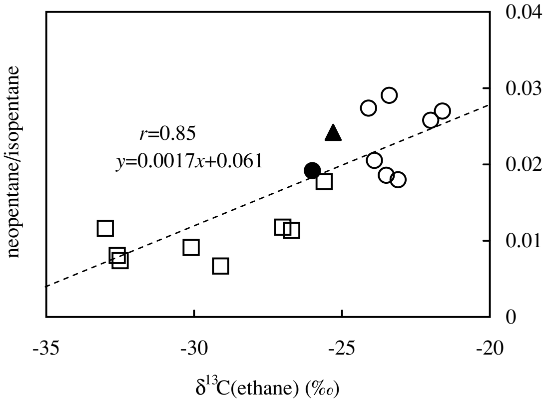

Fig. 1. Crossplot of δ^{13}C(ethane) and neopentane/isopentane ratio. Circle: samples from Niigata, Solid circle: a bacterial altered sample from Kubiki gas field in Niigata, Square: samples from Akita, Solid triangle: samples from Hokkaido.

RESULTS AND DATA

The methane, ethane, propane, isobutane, *n*-butane, neopentane, isopentane, *n*-pentane, 2,2-DMB, 2,3-DMB, 2-MP, 3-MP and *n*-hexane concentrations for the Yufutsu oil and gas field in Hokkaido, Japan are shown in Table 1. The δ^{13}C(ethane) data for the Yufutsu oil and gas field is also shown in Table 1.

The methane, ethane, propane, isobutane, *n*-butane, neopentane, isopentane and *n*-pentane data for the samples from Akita and Niigata, Japan are from Igari (1996) (Table 1). The 2,2-DMB, 2,3-DMB, 2-MP, 3MP and *n*-hexane data for the samples from Akita and Niigata are from Igari (2001) (Table 1). The δ^{13}C(ethane) data for the samples from Akita and Niigata are from Sakata (1991), Igari (1999a) and Igari (2001) (Table 1).

DISCUSSION

Relation between pentane and hexane isomer ratios and δ^{13}C(ethane)

Carbon isotopic composition of methane (δ^{13}C(methane)) has been often used as a gas maturation parameter (Schoell, 1983). However, the δ^{13}C(methane) changes by biogenic gas mixing. The δ^{13}C(ethane) is a better gas maturation parameter for thermogenic gas because it is usually unaffected by biogenic gas mixing (Igari, 1999a; Waseda *et al.*, 2002). The relation between the neopentane/isopentane ratio and δ^{13}C(ethane) is shown in Fig. 1. The neopentane/isopentane ratio increases with increasing δ^{13}C(ethane). It is known that the δ^{13}C (ethane) of natural gases in Akita and Niigata samples increases with an increase in the generation temperature (Igari, 1999a), implying that the neopentane/isopentane ratio also increases with the increase in the generation temperature. Equilibrium constants for neopentane/isopentane calculated by Eq. (1) are shown in Fig. 1, where T, absolute temperature; $K_{(T)}$, Equilibrium constant at T K; $\Delta G^{o}_{(T)}$, standard free energy change

Table 2. Bond dissociation energy and number of carbon atoms linked to the carbon atom forming the bond

	Bond dissociation energy (kJ/mol)	Number of carbon atoms linked to the carbon atom forming the bond
CH_3-CH_3	368	1
C_2H_5-CH_3	357	1
n-C_3H_7-CH_3	357	1
iso-C_3H_7-CH_3	351	2
n-C_4H_9-CH_3	360	1
iso-C_4H_9-CH_3	350	2
tertiary-C_4H_9-CH_3	344	3
neo-C_5H_{11}-CH_3	360	1

Data from The Chemical Society of Japan (1984).

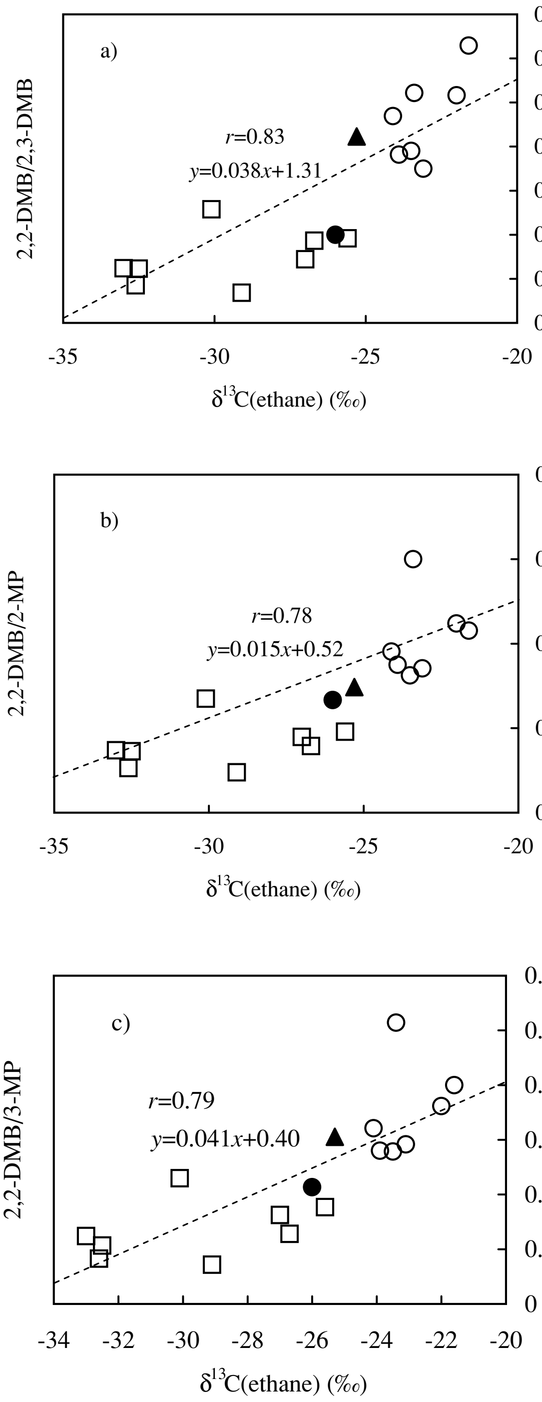

Fig. 2. Crossplot of δ^{13}C(ethane) and hexane isomer ratios. a) Crossplot of δ^{13}C(ethane) and 2,2/DMB/2,3DMB. b) Crossplot of δ^{13}C(ethane) and 2,2-DMB/2-MP. c) Crossplot of δ^{13}C(ethane) and 2,2-DMB/3-MP. Circle: samples from Niigata, Solid circle: a bacterial altered sample from Kubiki gas field in Niigata, Square: samples from Akita, Solid triangle: samples from Hokkaido.

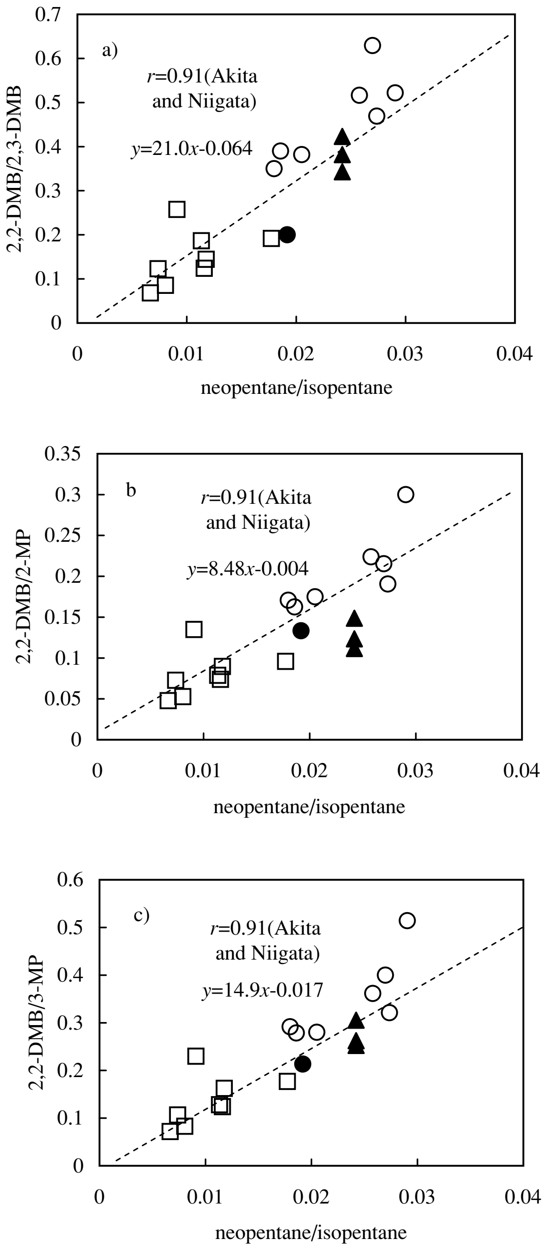

Fig. 3. Crossplot of neopentane/isopentane ratio and hexane isomer ratios. a) Crossplot of neopentane/isopentane and 2,2-DMB/2,3-DMB. b) Crossplot of neopentane/isopentane and 2,2-DMB/2-MP. c) Crossplot of neopentane/isopentane and 2,2-DMB/3-MP. Circle: samples from Niigata, Solid circle: a bacterial altered sample from Kubiki gas field in Niigata, Square: samples from Akita, Solid triangle: samples from Hokkaido.

at T K; R, gas constant. $\Delta G^{o}_{(T)}$ data are from Stull *et al.* (1969).

$$K_{(T)} = \exp(-\Delta G^{o}_{(T)}/RT). \qquad (1)$$

The equilibrium constant is 1.2 and 0.37 at 298 K and

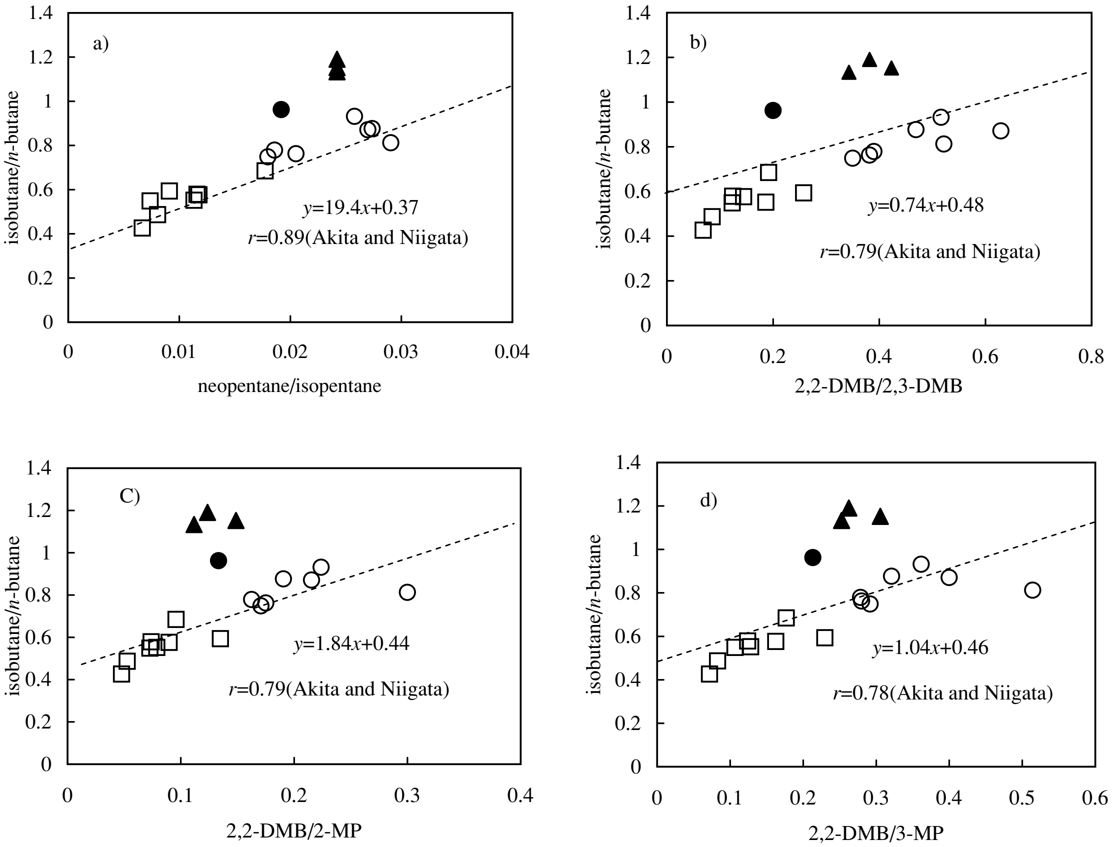

Fig. 4. Crossplot of pentane and hexane isomer ratios and isobutane/n-butane ratio. a) Crossplot of isopentane/neopentane and isobutane/n-butane. b) Crossplot of 2,2-DMB/2,3-DMB and isobutane/n-butane. c) Crossplot of 2,2-DMB/2-MP and isobutane/n-butane. d) Crossplot of 2,2-DMB/3-MP and isobutane/n-butane. Circle: samples from Niigata, Solid circle: a bacterial altered sample from Kubiki gas field in Niigata, Square: samples from Akita, Solid triangle: samples from Hokkaido.

400 K, respectively. Therefore, the neopentane and isopentane distributions of this study are not at equilibrium.

A C-C bond dissociation energy gets smaller as more carbon atoms are linked to the carbon atoms forming the bond (Table 2), showing that the bond dissociation energy of a C-kerogen bond becomes smaller as more carbon atoms are linked to the carbon atom. Furthermore, the bond dissociation energy also affects the activation energy. The ratio between reaction rates of neopentane dissociation and isopentane dissociation from kerogen is expressed by Eq. (2), where k, rate of dissociation reaction; A, frequency factor; E_{act}, activation energy.

$$k(\text{neopentane})/k(\text{isopentane}) = A(\text{neopentane})/A(\text{isopentane})\exp(E_{\mathrm{act}}(\text{isopentane}) - E_{\mathrm{act}}(\text{neopentane})/RT. \quad (2)$$

It is likely that $E_{\mathrm{act}}(\text{isopentane}) < E_{\mathrm{act}}(\text{neopentane})$ because the dissociation energy of isopentane is lower than that of neopentane (Table 2). Therefore, k(neopentane)/(isopentane) increases with increasing generation temperature. A crossplot of ratios among hexane isomers and δ^{13}C(ethane) is shown in Figs. 2a, 2b and 2c. The 2,2-DMB/2,3-DMB (Fig. 2a), 2,2-DMB/2-MP (Fig. 2b), 2,2-DMB/3-MP (Fig. 2c) ratios increase with increasing δ^{13}C(ethane). The explanation of these positive correlations is similar to that of neopentane/isopentane and δ^{13}C(ethane).

Relation between pentane isomer ratios and hexane isomer ratios

A crossplot of neopentane/isopentane and 2,2-DMB/2,3-DMB is shown in Fig. 3a. The samples from Akita and Niigata show a strong positive correlation ($r = 0.91$) because both ratios are affected by the generation temperature. Crossplots of neopentane/isopentane and 2,2-DMB/2-MP ratios, and neopentane/isopentane and 2,2-DMB/3-MP ratios are shown in Figs. 3b and 3c, respectively. They also show strong positive correlations. The

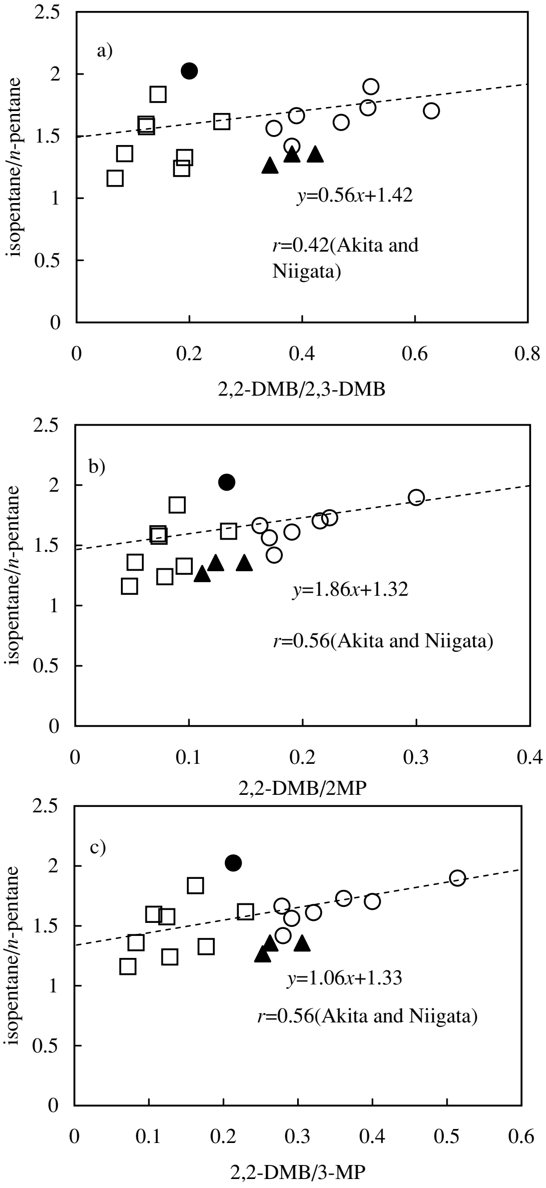

Fig. 5. Crossplot of hexane isomer ratios and isopentane/n-pentane ratio. a) Crossplot of 2,2-DMB/2,3-DMB and isopentane/n-pentane. b) Crossplot of 2,2-DMB/2-MP and isopenttane/n-pentane. c) Crossplot of 2,2-DMB/3-MP and isopentane/n-pentane. Circle: samples from Niigata, Solid circle: a bacterial altered sample from Kubiki gas field in Niigata, Square: samples from Akita, Solid triangle: samples from Hokkaido.

samples from Hokkaido show a little difference in Fig. 3b. The Hokkaido sample may be affected by other factors as described below.

Relation between pentane and hexane isomer ratios and isobutane/n-butane and isopentane/n-pentane ratios

The isobutane/*n*-butane ratio is also interrelated with the maturity for gases of Akita and Niigata (Kato, 1989). Crossplots of the pentane and hexane isomer ratios and isobutane/*n*-butane ratio are shown in Figs. 4a, 4b, 4c and 4d, where the Akita and Niigata samples show positive correlations. This crossplot shows that the isobutane/*n*-butane ratio increases with the increase of generation temperature. This trend cannot be explained only by the difference of bond dissociation energy between isobutane and *n*-butane. Although this isomer distribution is not well understood, preferential isomerization of *n*-butane to isobutane at high temperature is a possible explanation.

Generally, the gases of Hokkaido show a relatively high isobutane/*n*-butane ratio in Figs. 4a, 4b, 4c and 4d. The source kerogen is type II for Akita and Niigata, and type III for Hokkaido (Waseda *et al.*, 2002). Therefore, kerogen type also affects the isobutane/*n*-butane ratio. This is in accord with the result of Yonetani (1986). In addition, the high isobutane/*n*-butane ratio could also be caused by bacterial degradation. Through bacterial degradation, *n*-alkanes are selectively degraded (James and Burns, 1984; Waseda *et al.*, 2002). A sample from Kubiki (Kuroi) gas field in Niigata is degraded by bacteria (Sakata, 1991; Igari, 1999b). The same sample also shows a high isobutane/*n*-butane ratio in Figs. 4a, 4b, 4c and 4d.

Crossplots of the hexane isomer ratios and isopentane/*n*-pentane ratio are shown in Figs. 5a, 5b and 5c. Weak positive correlations are observed between hexane isomer ratios and isopentane/*n*-pentane ratio. A bacterial altered sample shows a high isopentane/*n*-pentane ratio, however the gases from Hokkaido do not show a high isopentane/*n*-pentane ratio. It shows that gases from Hokkaido are not degraded by bacteria. Therefore, higher isobutane/*n*-butane ratios of the gases from Hokkaido may be due to kerogen type III.

As shown in Figs. 3a, 3b and 3c, pentane and hexane isomer ratios of the Kubiki sample are not different from other samples from Akita and Niigata. It shows the ratios are not affected by bacterial degradation compared with the isobutane/*n*-butane ratio. Therefore, the pentane and hexane isomer ratios of natural gases are inferred to be more effective parameters of gas generation temperature compared to the isobutane/*n*-butane ratio.

CONCLUSIONS

Abundance ratios of pentane and hexane isomers in natural gases are discussed in detail for the first time. The neopentane/isopentane ratio has good positive correlations with the δ^{13}C(ethane) as well as 2,2-DMB/2,3-DMB, 2,2-DMB/2-MP and 2,2-DMB/3-MP ratios, being affected by generation temperature. On the other hand, the isobutane/*n*-butane ratio has weak correlations with these parameters, which is probably influenced by the kerogen type.

Carbon isotopic ratios of ethane and propane have been used as good parameters for gas generation temperature. Pentane and hexane isomer ratios are should also be good parameters. The combination of carbon isotopic ratios and pentane and hexane isomer ratios are expected to be more effective parameters for the gas generation temperature.

Acknowledgments—We are grateful to the Japan Petroleum Exploration Co. for supplying samples for this study. We are thankful to anonymous reviewers for constructive comments on the manuscript.

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