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Semi-open and closed system pyrolysis of Paleogene coal for evaluating the timing of hydrocarbon gas expulsion

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Abstract

Hydrocarbon gas expulsion from coal source rocks takes place under conditions intermediate between an open and closed system. The compositional and isotopic changes of hydrocarbon gases generated from Paleogene coal with increasing maturation were investigated under semi-open and closed system laboratory pyrolysis to evaluate the maturity level at the time of hydrocarbon gas expulsion. Lower yields of saturated hydrocarbon gases and their higher $\delta^{13}C$ values were observed in the semi-open system pyrolysis compared to those at the same maturity level in the closed system pyrolysis, since gaseous hydrocarbons depleted in ^{13}C were removed during semi-open system pyrolysis. The $\delta^{2}H$ values of hydrocarbon gases generated in the closed system pyrolysis were initially lower than those in the semi-open system pyrolysis, and then became markedly higher at the higher maturity level (vitrinite reflectance [VR_r] > 1.2%), indicating significant hydrogenation of isotopically heavier inorganic hydrogen derived from water moisture in the coal matrix. The semi-open and closed system pyrolysis showed that the relationship between the isotopic composition of hydrocarbon gases expelled from coal and the maturity of coal depends on the state of openness or closedness of the hydrocarbon generation environment. Diagrams showing the relationship between the $\delta^{13}C$ values of hydrocarbon gases expelled from

Paleogene coal and the VR_r under conditions intermediate between semi-open and semi-closed systems were proposed for evaluating the timing of hydrocarbon gas expulsion in sedimentary basins.

Keywords:

Paleogene coal; carbon and hydrogen isotopic compositions; hydrocarbon gas expulsion, open and closed system pyrolysis

1. Introduction

The enrichment of ^{13}C in thermogenic hydrocarbon gases, such as methane (C_1), ethane (C_2) and propane (C_3), with increasing maturation has been well studied in the laboratory and applied to the evaluation of the maturity level of natural gas (e.g., Clayton, 1991; Berner et al., 1992, 1995; Andresen et al., 1995; Berner and Faber, 1996; Michels et al., 2002). In the case of accumulated hydrocarbon gases in a reservoir, in many cases, the maturity level of the gases is related to the timing of gas expulsion from the source rocks if there is no thermal alteration after accumulation. The burial depth and temperature at the time of the expulsion in deep sedimentary basins are often recorded for natural gas according to its maturity level. The stable carbon and hydrogen isotopic composition ($\delta^{13}C$ and $\delta^{2}H$) of gaseous hydrocarbons represents one of only a few indicators for evaluating the maturity level of natural gas. The $\delta^{13}C$ and $\delta^{2}H$ values of hydrocarbon gases in reservoir rocks can therefore indicate the timing of the expulsion of the gas from coal seams.

In previous studies, laboratory pyrolysis experiments on coal have been performed to elucidate the progressive change in the $\delta^{13}C$ values of coal-derived hydrocarbon gases with increasing maturation. These pyrolysis experiments can be classified into open system pyrolysis (e.g., Berner et al., 1995; Cramer et al., 1998,

2001; Gaschinitz et al., 2001), anhydrous closed system pyrolysis (e.g., Liu et al., 2007; Duan et al., 2012; Li et al., 2013, 2016; Takahashi et al., 2014), and hydrous closed system pyrolysis (e.g., Chung and Sackett, 1979; Andresen et al., 1995; Kotarba and Lewan, 2004). Under open system pyrolysis, secondary cracking does not occur, or is very limited, since volatile pyrolyzates generated by the primary cracking of organic matter are immediately removed from the reaction system. In contrast, secondary and tertiary cracking of pyrolyzates proceed further under closed system conditions. If hydrocarbon generation in the source rocks proceeds under open system thermal maturation, the expulsion of hydrocarbon gas from the source rocks takes place efficiently. However, if hydrocarbon generation proceeds under closed system conditions, hydrocarbon gas expulsion does not takes place due to the retention of thermogenic products in the source rocks. In the natural environment, it is more likely that the source rocks are restricted during their evolution by neither fully open nor fully closed systems, and the generation and expulsion of hydrocarbon gases in the sedimentary basin proceed under conditions intermediate between an open and closed system. If the changes in the $\delta^{13}C$ and $\delta^{2}H$ values of hydrocarbon gases with thermal maturation under both open and closed system conditions are known, the timing of hydrocarbon gas expulsion from the coal source rocks can be estimated more accurately

based on the carbon and hydrogen isotopic compositions of natural hydrocarbon gas.

Open system pyrolysis is generally performed under inert gas flow. In the present study, semi-open system pyrolysis was used to estimate the progressive changes in the $\delta^{13}C$ and $\delta^{2}H$ values of hydrocarbon gases and the vitrinite reflectance (VR_r) of the source coal with thermal maturation. We performed the semi-open system pyrolysis according to Michels et al. (2002), as follows. The coal sample was pyrolyzed in the reaction chamber under closed system conditions, and the free gases generated from the coal were recovered after completion of the pyrolysis. The remaining coal sample was then re-pyrolyzed at a higher temperature than in the previous pyrolysis experiment. The experimental process was repeated until the final pyrolysis experiment at the highest temperature. This series of pyrolysis experiments is known as semi-open system pyrolysis. Experiments of semi-open and closed system pyrolysis of coal can reveal the influence of the openness or closedness of the reaction environment on the relationship between the $\delta^{13}C$ and $\delta^{2}H$ values of hydrocarbon gases released from the coal, as well as the maturity level of the source coal. Changes in the isotopic composition of hydrocarbon gases from Paleogene coal with increasing thermal maturation under semi-open and closed system conditions provide useful datasets for evaluating the timing of hydrocarbon gas expulsion from coal source rocks.

2. Materials and methods

2.1. Samples

Eocene coal-bearing strata are distributed widely from north to south in the Ishikari sedimentary basin in central Hokkaido. The middle to late Eocene Ishikari Group comprises the major stratigraphic sequence in the basin. The Ishikari Group consists of mainly non-marine to littoral sedimentary rocks with abundant coal seams, which have been exploited as the Ishikari coal field since the late 19th century. The Ishikari Group is divided into nine lithostratigraphic formations (Imai, 1924). A coal sample was taken from outcrops of one of the formations exposed at Yubari, the Middle Eocene Yubari Formation, which is composed of alternating beds of sandstone, mudstone, and coal seams deposited in fluvial and floodplain to estuarine environments (Takano and Waseda, 2003). The Eocene coals in the Ishikari basin are important source rocks of the Yufutsu oil and gas field (Waseda et al., 1998; Yessalina et al., 2006).

The Eocene Yubari coal is composed mainly of vitrinite, with small amounts of degradinite (detrovitorinite) macerals. The VR_r, and organic carbon, hydrogen, total nitrogen and total sulfur contents, of the Eocene Yubari coal used in the present study are shown in Table 1. Takahashi et al. (2014) reported the changes in the concentrations

and isotopic compositions of gas components generated from the same Eocene Yubari coal source under anhydrous closed system pyrolysis. The elemental composition and VR_r of artificially matured coals obtained by anhydrous closed system pyrolysis of Eocene Yubari coal are shown in Table 1. The bulk carbon isotopic composition of the Yubari coal sample was determined by SI Science Co. (Japan) to be –24.0‰.

2.2. Semi-open system pyrolysis of coal

Semi-open system pyrolysis experiments were conducted using a 30-mL reactor made of stainless steel 316 (Nitto Koatsu, Co., Ltd, Japan). The Yubari coal sample was crushed to fragments of 5–7 mm and dried at 60ºC for 24 h. Approximately 5 g of coal fragment sample was used in each pyrolysis experiment. The reactor was evacuated for several minutes and subsequently purged with He gas for 5 min. The reactor was then heated rapidly to the pyrolysis temperature, and the temperature was held constant for 72 h in a GC-14A oven (Shimadzu Co., Japan). The pyrolysis temperature was carefully monitored using a thermometer to an accuracy of within ±0.5ºC. The gaseous products generated from the individual coal samples, each pyrolyzed at 330, 340, 350, 370, and 390ºC for 72 h, were sequentially collected in aluminum bags as samples that had undergone semi-open system pyrolysis. Higher

pyrolysis temperature and shorter reaction time in the artificial maturation of coal are assumed to be kinetically comparable to low temperature and long-term heating in a sedimentary basin. The oven was cooled below 100ºC before gas sampling. The pyrolysis gas expelled from the coal fragments was collected using a 1.0-L aluminum bag (GL Science Co.), and the total volume of expelled gas was measured at room temperature using a 100-mL gastight syringe (GL Science Co.).

2.3. Gas analysis

The composition of the gases from the semi-open system was measured by gas chromatography (GC) using an Agilent 7890A instrument (USA) equipped with a pulsed discharge helium ionization detector (PDHID) and a micropacked column containing ShinCarbon-ST 80/100 (2.0 m × 1.0 mm i.d.; Shinwa Co., Japan). The oven temperature for the GC was initially programmed at 40ºC for 3 min, increasing to 300ºC at 15ºC/min, and then held at 300ºC for 15 min. Ultra-high purity He was used as the carrier gas. A constant amount of gas was introduced into the GC column using a 10-µL sampling loop. Compounds were identified by comparing the retention times with those of reference standards in a gas mixture containing CH_4, C_2H_4, C_2H_6, C_3H_6, C_3H_8, *i*-C_4H_{10}, *n*-C_4H_{10}, H_2, CO, and CO_2. The detailed analytical method, as well as the

method for identification of the gases, are described in Saito et al. (2012).

2.4. Isotope analysis

Stable carbon isotopic analysis was performed by GC-combustion-isotope ratio mass spectrometry (GC-C-IRMS, Agilent 6890A GC and Finnigan [Germany] MAT 252) using the same micropacked column (ShinCarbon-ST 80/100, 2.0 m × 1.0 mm i.d.; Shinwa Co.) and He as the carrier gas. The GC oven temperature was programmed to 40ºC for 3 min, then to 300ºC at 15ºC/min, and finally held at 300ºC for 20 min. The combustion was performed in a micro-volume ceramic tube with CuO, NiO, and Pt wires at 900ºC. The stable hydrogen isotopic composition was measured using GC-high-temperature conversion–isotope ratio mass spectrometry (GC-HTC-IRMS; Finnigan Delta V Advantage) using the same micropacked column and He as the carrier gas. The oven temperature program was the same as that for the GC-C-IRMS. The thermal conversion furnace between the GC and IRMS was maintained at 1,450ºC. Stable carbon and hydrogen isotope data were recorded as δ^{13}C and δ^{2}H values relative to the VPDB and VSMOW scales, respectively, according to Coplen (2011). The δ^{13}C and δ^{2}H values were determined based on a single-point calibration by comparison with the MZ3-01 CH_4 standard (δ^{13}C of -31.1‰; SI Science Co., Japan) and the Indiana CH_4

#1 standard ($\delta^{13}C$ of -38.85‰ and $\delta^{2}H$ of -160.8‰; Indiana University, USA), respectively. The $\delta^{13}C$ value of the MZ3-01 CH_4 standard has been calibrated against NBS 19. The $\delta^{13}C$ and $\delta^{2}H$ values of the Indiana CH_4 #1 standard are normalized to NBS 19/L-SVEC and VSMOW/SLAP, respectively. The H_3^+ factor of the mass spectrometer was determined once daily using external reference gas injections and was consistently < 10 ppm. Selected gas samples were measured repeatedly for $\delta^{13}C$ and $\delta^{2}H$ three to five times. The results showed that the analytical precisions of the $\delta^{13}C$ and $\delta^{2}H$ values were within ±0.5‰ and ±10‰, respectively.

2.5. Measurement of vitrinite reflectance

The VR_r was measured using a reflecting microscope (Eclipse LV100ND; Nikon, Ltd., Japan) equipped with a stabilized halogen light source and photonic multichannel analyzer (PMA12; Hamamatsu Photonics Co., Japan). The VR_r value was measured for a spot diameter of 20 μm at a wavelength of 542.8 nm by comparison with the standard values of polished glasses with VR_r values of 0.55, 0.79, 1.08, and 1.53%. The VR_r value of the coal samples was determined based on a VR_r dataset obtained from 40 to 50 spots. The accuracy of the VR_r measurements was within ±0.03% for a VR_r range of 0.3–2.0%.

3. Results and discussion

3.1. Changes in gas yields with maturation

The gaseous hydrocarbons and non-hydrocarbons generated from the Eocene Yubari coal during semi-open system pyrolysis were CH_4 to *n*-C_4H_{10} (C_1 to C_4), C_2H_4, C_3H_6, *i*-C_4H_{10}, H_2, CO, and CO_2. Typical PDHID gas chromatograms for these gas components are shown in Fig. 1. The O_2 and N_2 in the chromatograms were contaminants from the air. C_1 was generally the most abundant hydrocarbon gas in the pyrolysis product. The relative abundance of C_2 to C_3 increased with increasing heating temperature, showing the progress of thermal cracking. The significant decrease in CO_2 with heating temperature was due to the rapid removal of oxygen-containing functional groups. The independent yields and cumulative yields (the sum of independent yields in each pyrolysis experiment) of the gas components in the series of semi-open system pyrolysis experiments are shown in Table 2. The VR_r values for coal samples pyrolyzed in the semi-open system (Table 2) were obtained from the measured VR_r values for coal samples pyrolyzed in the closed system (Table 1) under the same time-temperature conditions as those for the corresponding individual semi-open system pyrolysis. Taking into account the longer reaction time due to the multiple and sequential pyrolysis

processes, the VR_r values in the semi-open system pyrolysis were slightly higher than those in the corresponding closed system pyrolysis. However, this difference was almost negligible in the context discussed below. The independent and differential yields (the difference in the yield of the gas component between two successive pyrolysis experiments) of gas components in the series of closed system pyrolysis experiments are shown in Table 3. Changes in the cumulative yield of the gas components of the semi-open system pyrolysis and in the independent yield of the gas components of the closed system pyrolysis with increasing VR_r are shown in Fig. 2.

The yields of saturated hydrocarbon gases (C_1, C_2 and C_3) in the closed system pyrolysis were similar to the cumulative yields of hydrocarbon gases in the semi-open system pyrolysis at the lower maturity level ($VR_r < 1.2\%$) (Fig. 2). However, they were clearly higher than the cumulative yields of hydrocarbon gases in the semi-open system pyrolysis at the higher stage of maturation ($VR_r > 1.2\%$). This was due to the removal of gaseous hydrocarbons, which can be a source of C_1, C_2 and C_3, from the reaction chamber during the series of semi-open system pyrolysis. Unsaturated hydrocarbons, such as C_2H_4 and C_3H_6, were comparatively minor compounds. These unsaturated hydrocarbons were more abundant in pyrolyzates from the semi-open system pyrolysis compared to those from the closed system pyrolysis. The abundance of unsaturated

hydrocarbons was related to the degree of saturation by hydrogenation during the pyrolysis experiment. Lower abundance of unsaturated hydrocarbons in the pyrolyzates from the closed system pyrolysis suggested that the process of hydrogenation to alkenes proceeded more efficiently in the closed system pyrolysis. The abundance of H_2 in the reaction chamber of the closed system pyrolysis was higher than that of the semi-open system pyrolysis at the same maturation level, since H_2 was removed from the reaction chamber during the series of semi-open system pyrolysis. The lower concentration of unsaturated hydrocarbons in the closed system pyrolysis can be interpreted as being due to efficient hydrogenation, owing to the higher H_2 concentration in the reaction chamber of the closed system pyrolysis. However, the cumulative yields of CO_2 from the semi-open system pyrolysis increased significantly at the lower maturity level (VR_r < 0.7%), while the yields of CO_2 from the closed system pyrolysis increased significantly at the relatively higher maturity level (VR_r > 1.2%). The CO_2 in the thermogenic gas was derived from oxygen-containing functional groups, such as carbonyl and carboxyl groups. The fairly scattered plot for the yield of CO_2 from the closed system pyrolysis could be due to the adsorption of CO_2, on the surface of the coal sample and on the inner surface of the reaction chamber, during gas sampling collection into the aluminum bag. The CO_2 yield of the first semi-open system pyrolysis at 330ºC for 72 h was

significantly higher than that of the closed system pyrolysis under the same conditions, indicating the uncertainty in determining the CO_2 yield. Lewan (1997) reported that a trace amount of water vapor in the anhydrous pyrolysis experiments could oxidize carbonyl groups to form carboxyl and hydrogen. Decarboxylation is one of the major sources of CO_2. The higher CO_2 yield in the closed system pyrolysis at the higher maturity level was attributable to a higher water vapor concentration in the closed system pyrolysis, since water vapor was removed from the reaction chamber during the semi-open system pyrolysis.

3.2. Changes in carbon isotopic composition with maturation

In the semi-open system pyrolysis, the volatile products generated from the individual coal samples pyrolyzed at 330, 340, 350, 370, and 390ºC for 72 h were collected sequentially. The mean VR_r value marking the maturity level of the hydrocarbon gases from the independent semi-open system pyrolysis was the logarithmic mean determined using the two VR_r values of successive semi-open system pyrolysis. The $\delta^{13}C$ values of the hydrocarbon gases from the semi-open system can be assumed to represent those of the hydrocarbon gases expelled from the coal source rocks under the open system at the mean VR_r value. The mean VR_r and $\delta^{13}C$ values of

the hydrocarbon gases from the semi-open system are shown in Table 4.

Hydrocarbon gas expulsion does not take place under fully closed systems. The expulsion of hydrocarbon gases is thought to take place under conditions close to an open system in the early stage of diagenesis because of the comparatively high porosity and permeability of the coalbed, and significant water expulsion with increasing compaction. Hydrocarbon gas expulsion proceeds gradually under conditions closer to a closed system with the lower porosity and permeability of the coalbed in the later stages of diagenesis. Hydrocarbon gas expelled from the coal under the semi-closed system is therefore a mixed gas of newly-generated and pre-generated hydrocarbon gases, which is poor in the hydrocarbon gases generated in the early stage of diagenesis. The differential hydrocarbon gases of the successive closed system pyrolysis in the present study (Table 3) were composed of a hydrocarbon gas mixture without the gas generated in the early stage of pyrolysis, similar to the hydrocarbon gas expelled from the coal under the semi-closed system. The apparent $\delta^{13}C$ value of the differential hydrocarbon gas in the series of closed system pyrolysis experiments was estimated based on the extrapolated difference in the $\delta^{13}C$ value and volume of hydrocarbon gas between two successive pyrolysis experiments (Table 5). The measured VR_r corresponding to each closed system pyrolysis was used as the maturity level of the hydrocarbon gas expelled

from the coal under the semi-closed system (Table 5). The changes in the $\delta^{13}C$ values of C_1, C_2, and C_3 ($\delta^{13}C_1$, $\delta^{13}C_2$, and $\delta^{13}C_3$), which were assumed to represent those expelled from Eocene Yubari coal under the semi-open and semi-closed systems with increasing VR_r, are shown in Fig. 3.

The $\delta^{13}C_1$ value was generally lower than the $\delta^{13}C_2$ and $\delta^{13}C_3$ values. The observed relationship of $\delta^{13}C_1 < \delta^{13}C_2 < \delta^{13}C_3$ is characteristic for thermogenic hydrocarbon gases (e.g., McCarty and Felbeck, 1986; Chung et al., 1988; Liguo et al., 2009). The $\delta^{13}C_1$, $\delta^{13}C_2$, and $\delta^{13}C_3$ values of the expelled gas under the semi-open system increased with increasing maturation, although a decrease in the $\delta^{13}C_1$ value in the initial stage of coal maturation ($VR_r < 0.9\%$) was also observed (Fig. 3). The $\delta^{13}C$ value of CH_4 generated in the initial stage of the pyrolysis experiments is often high (e.g., Berner and Faber, 1996; Cramer et al., 1998; Takahashi et al., 2014). According to Chung and Sackett (1980) and Smith et al. (1985), the initial thermogenic CH_4 is thought to be generated from a pool of isotopically heavy methyl groups bound to relatively labile C–O or C–S linkages. $\delta^{13}C_1$ then becomes lighter in the initial stage of pyrolysis and subsequently becomes heavier again with increasing pyrolysis temperature in the higher maturation stage ($VR_r > 0.9\%$). Enrichment of ^{13}C in natural gas with increasing temperature has been well documented (e.g., Clayton, 1991;

Andresen et al., 1995; Cramer et al., 1998; Tang et al., 2000). The increase in $\delta^{13}C_1$ in the higher maturation stage is due to the mixing of CH_4 generated from isotopically heavier and more tightly bound aliphatic structures in kerogen and bitumen. A comparison of the $\delta^{13}C$ values of hydrocarbon gases expelled under the semi-open and semi-closed systems at the same VR_r showed that the former were higher than the latter at the maturity level of VR_r > 0.7% (Fig. 3). The difference in the $\delta^{13}C$ value between the semi-open and semi-closed systems increased with increasing maturation. Hydrocarbon gases rich in ^{12}C pre-generated under the closed system were mixed with the newly-generated ones to form the expelled gas rich in ^{12}C, while in the case of the semi-open system, pre-generated hydrocarbon gases rich in ^{12}C were removed from the semi-open system to form the expelled gas composed mainly of newly-generated hydrocarbon gases depleted in ^{12}C. The higher $\delta^{13}C$ values of hydrocarbon gases expelled from the semi-open system were due to the removal of pre-generated hydrocarbon gases rich in ^{12}C from the reaction system.

3.3. Changes in hydrogen isotopic composition with maturation

Tables 4 and 5 show the δ^2H values of C_1, C_2 and C_3 (δ^2H_{C1}, δ^2H_{C2} and δ^2H_{C3}) expelled from the Eocene Yubari coal under the semi-open and semi-closed systems,

respectively. The δ^2H values were measured in the hydrocarbon gases obtained from each pyrolysis experiment for the semi-open system. In the semi-closed system, the δ^2H values of the hydrocarbon gases were the apparent values calculated for the differential hydrocarbon gases, as described above for the apparent δ^{13}C values of the differential hydrocarbon gases. The δ^2H_{C1}, δ^2H_{C2} and δ^2H_{C3} values tended to increase with increasing VR_r, although they decreased, or did not change significantly, in the initial stage of maturation (Fig. 4).

The δ^2H values of thermogenic hydrocarbon gases can be controlled by the hydrogenation of radicals and double bonds. The δ^2H value of hydrogen released by cleavage of the C–H bond increases with increasing thermal maturation, since the dissociation energy of the C–^{2}H bond is higher than that of the C–H bond. Therefore, the δ^2H values of thermogenic hydrogen increase with increasing thermal maturation. However, the δ^2H values of the hydrocarbon gases in both the semi-open and semi-closed systems did not change significantly in the early stage of maturation (VR_r < 1.0%), indicating that hydrogenation did not affect the δ^2H value of the hydrocarbon gases in this stage. The δ^2H value of the hydrocarbon gases subsequently increased with increasing maturation, suggesting that hydrogenation of isotopically heavier hydrogen was occurring at the higher maturation stage. The rate of increase in the δ^2H value of the

hydrocarbon gases in the semi-closed system was remarkably high compared to that in the semi-open system. The different rate of increase in the δ^2H value was attributable to the different concentrations of hydrogen between the semi-open and semi-closed systems. The hydrogenation of radicals and double bonds proceeded more efficiently in the semi-closed system pyrolysis than in the semi-open system pyrolysis, since the hydrogen concentration in the reaction system of the semi-closed system pyrolysis was always greater than that of the semi-open system. This is evidenced by lower concentrations of unsaturated C_2H_4 and C_3H_6 in the closed system pyrolysis compared to those in the semi-open system pyrolysis (Fig. 2).

Another possible reason for the higher δ^2H value of the hydrocarbon gases in the semi-closed system is that the hydrogen in the reaction chamber of the closed system pyrolysis was partly composed of isotopically heavier hydrogen derived from water moisture in the coal matrix. Hydrogen derived from water can contribute directly to the hydrogenation of radicals and double bonds simultaneous with hydrocarbon generation (e.g., Seewald, 1994; Lewan, 1997; Schimmelmann et al., 1999, 2001). The δ^2H value of inorganic hydrogen (water-derived hydrogen) is generally higher than that of organic hydrogen. Water vapor was removed from the reaction chamber with gas samples during the sampling stage of the semi-open system pyrolysis, while isotopically

heavier hydrogen derived from water moisture remained in the reaction chamber. The remarkable increase in the δ^2H values of the hydrocarbon gases at the later stage of maturation (VR_r > 1.2%) in the semi-closed system could be due to the significant incorporation of hydrogen derived from water moisture.

The relationship of $\delta^2H_{C1} < \delta^2H_{C2} < \delta^2H_{C3}$ was observed, similar to the relationship among the $\delta^{13}C_1$, $\delta^{13}C_2$, and $\delta^{13}C_3$ values (Figs. 3 and 4). The dissociation energy of the C–C bond with ^{2}H is larger than that without ^{2}H (e.g., Schoell, 1980). The lowest δ^2H_{C1} value is thought to be because the C–C bond without ^{2}H is more easily broken compared to that with ^{2}H. Ni et al. (2011) proposed a kinetic model of hydrogen isotope fractionation during the generation of hydrocarbon gases based on quantum chemistry calculations for *n*-octane homolytic cracking. This kinetic model could be applicable to evaluation of the maturity level of natural gas. However, hydrogen exchange between interstitial water and sedimentary organic matter in the early stage of diagenesis has also been suggested as a possible mechanism (Schimmelmann et al., 1999, 2001; Lis et al., 2006; Kikuchi et al., 2010). The δ^2H of higher land plants is also related to the climate humidity or aridity (e.g., Tipple and Pagani, 2010; Duan et al., 2011b; Yang et al., 2011). Estimation of the kerogen type of source rocks, and the maturity level of hydrocarbon gases at the time of hydrocarbon gas expulsion from the

source rocks based on the hydrogen isotopic composition, requires caution.

3.4. Evaluation of the timing of gas expulsion from coal

Oil and gas fields distributed in Southeast Asia are frequently associated with Cenozoic coal fields, where coal and coaly strata are important source rocks of oil and gas (e.g., Hoffmann et al., 1984; Waseda and Nishita, 1998; Hossain et al., 2014). Cenozoic coals have the potential to generate oil, since they are relatively rich in hydrogen and aliphatic structures compared with older Carboniferous coals (e.g., Aihara, 1979; Takahashi and Aihara, 1989; MacGregor, 1994; Petersen and Nytoft, 2006; Petersen et al., 2009). The maturity level of hydrocarbon gases in reservoirs generally indicates the maturity level at the time of their expulsion from the source rocks. Therefore, the relationship between the $\delta^{13}C$ values of hydrocarbon gases and VR_r can be applicable to evaluation of the timing of hydrocarbon gas expulsion from the coaly source rocks. Changes in the $\delta^{13}C$ values of hydrocarbon gases from older pre-Cenozoic coals (Type III kerogen) with increasing maturation have been comparatively well studied in the laboratory (e.g., Arneth and Matzigkeit, 1986; Liu et al., 2007; Duan et al., 2011a; Li et al., 2013, 2016). However, the relationship between the $\delta^{13}C$ values of C_1, C_2 and C_3 expelled from hydrogen-rich Cenozoic coal and the VR_r of the source coal is

still poorly understood. In addition, to date, laboratory experiments relating to changes in the $\delta^{13}C$ values of C_1, C_2 and C_3 with maturation have not examined the conditions under which the expulsion of hydrocarbon gases from the coal occurs. The relationship between the $\delta^{13}C$ values of the hydrocarbon gases and VR_r, which is often applied in oil and gas exploration, is based on open system pyrolysis (e.g., Berner et al., 1995; Berner and Faber, 1996; Cramer et al., 2001). However, it is reasonable to assume that hydrocarbon gas expulsion in sedimentary basins occurs under conditions intermediate between those of open and closed systems.

Figure 5 shows a diagram of the relationship between the $\delta^{13}C$ values of C_1, C_2 and C_3 expelled from Cenozoic coal and the VR_r of the source coal at the time of gas expulsion, based on the experimental results (Fig. 3) of the semi-open and closed system pyrolysis in this study. In the sedimentary basin, the expulsion of hydrocarbon gases in the early stage of diagenesis is thought to take place under conditions close to an open system (semi-open system). The expulsion of hydrocarbon gas proceeds gradually under conditions closer to a closed system (semi-closed system), with decreasing porosity and permeability of the coalbed in the later stage of diagenesis. Therefore, in the major stage of gas expulsion from coal seams, newly generated hydrocarbon gases are mixed with pre-generated coalbed gas, and some of the mixed

gas is expelled from the coal seams under the semi-closed system. The $\delta^{13}C$ value of the hydrocarbon gases expelled from the coal under the semi-open system was generally higher than that in the gases expelled under the semi-closed system at the same maturity level (Fig. 3), since the hydrocarbon gases expelled under the semi-open system did not contain pre-generated hydrocarbon gases depleted in ^{13}C. The expulsion of hydrocarbons from the coal source rocks in sedimentary basins generally proceeds under conditions intermediate between semi-open and closed system. Therefore, the evolutionary path of the $\delta^{13}C$ values of hydrocarbon gases expelled from the coal source rocks should be located between the paths of evolution under semi-open and semi-closed systems shown in Fig. 5. Natural gas from the Yufutsu oil and gas field in Hokkaido is derived from Paleogene coals (Waseda and Nishita, 1998). Waseda et al. (2002) reported $\delta^{13}C$ values of hydrocarbon gases of $\delta^{13}C_1$ = -35.3‰, $\delta^{13}C_2$ = -25.6‰, and $\delta^{13}C_3$ = -23.6‰. These values are plotted along evolutionary paths of $\delta^{13}C$ in Fig. 5, and were consistent with the results of our laboratory pyrolysis experiments. The carbon isotopic composition of natural gas from the Yufutsu oil and gas field lies close to the evolutionary paths of the $\delta^{13}C$ values of the hydrocarbon gases expelled under the semi-open system, suggesting that hydrocarbon gas expulsion from the coal source rocks in the sedimentary basin is occurring under conditions close to a semi-open

system.

In addition, the isotopic compositions of hydrocarbon gases reflect post-genetic phenomena, such as expulsion, migration, biodegradation, and mixing. The carbon isotopic fractionation that occurs during expulsion of CH_4 in coals and total organic carbon (TOC)-rich shales can affect the isotopic fractionation of CH_4 (e.g., Prinzhofer and Huc, 1995; Prinzhofer and Pernaton, 1997; Zhang and Krooss, 2001; Takahashi et al., 2014), although the carbon isotopic fractionation of C_2 and C_3 during their expulsion from coal has been reported as almost negligible (Takahashi et al., 2014). The $\delta^{13}C$ value of C_1 in the reservoir decreases due to the biodegradation of oil and the mixing of microbial C_1, which is significantly depleted in ^{13}C. Although the $\delta^{13}C$ value of biogenic C_2 is also much lower than that of thermogenic C_2 (Mattavelli et al., 1992; Waseda and Didyk, 1995), the amount of biogenic C_2 is very limited (Oremland et al., 1988). Evaluation of the maturity level of natural gas based only on the $\delta^{13}C$ value of C_1 requires caution. The $\delta^{13}C$ value of the thermogenic gas is also related to the $\delta^{13}C$ value of the source organic matter. The $\delta^{13}C$ value of the bulk Eocene Yubari coal used for our pyrolysis experiments was –24‰ (VR_r = 0.46%) (Table 1). The $\delta^{13}C$ value of the source organic matter should be taken into account at the time of application of the relationship between the $\delta^{13}C$ values of C_1, C_2 and C_3, and VR_r shown in Fig. 5. The diagrams

shown in Fig. 5 should be verified by empirical studies. However, the conceptual view in Fig. 5 is useful for assessment of the maturity of natural gas, and is applicable to the evaluation of the timing of gas expulsion from coal in the sedimentary basin.

4. Conclusions

In this study, we investigated the compositional and isotopic changes of hydrocarbon gases generated from Paleogene coal with increasing maturation under semi-open and closed system laboratory pyrolysis. The different experimental conditions, i.e., semi-open or closed system, were well represented in the compositional and isotopic changes of the hydrocarbon gases with thermal maturation. The increases in the $\delta^{13}C$ values of C_1, C_2 and C_3 under the semi-open system pyrolysis were greater than those under the closed system pyrolysis, since volatile hydrocarbon gases depleted in ^{13}C were intermittently removed from the reaction chamber during the semi-open system pyrolysis. The relationship between the $\delta^{13}C$ values of the hydrocarbon gases expelled from the coal and the VR_r of the source coal depended on the state of openness or closedness of the reaction environment. Therefore, evaluation of the maturity level of hydrocarbon gases, based on their isotopic composition, should take into consideration the state of openness or closedness of the coal source rocks during burial diagenesis.

Diagrams showing the relationship between the $\delta^{13}C$ values of C_1, C_2 and C_3 and VR_r of the source coal were drawn based on the experimental results from the semi-open and closed system pyrolysis. The $\delta^{13}C$ values of C_1, C_2 and C_3 with increasing VR_r should fall between the two paths of evolution of $\delta^{13}C$ versus VR_r obtained by semi-open and closed system pyrolysis, since the expulsion of hydrocarbon gas from the coal takes place under conditions intermediate between a semi-open and closed system. Interpretation of the diagrams is useful for evaluating the maturity level of hydrocarbon gases and the timing of their expulsion from the coal source rocks in sedimentary basins.

The $\delta^{2}H$ values of hydrocarbon gases generated under the closed system pyrolysis increased significantly at the higher maturity level (VR_r > 1.2%). We suggest that this was due to significant hydrogenation of isotopically heavier inorganic hydrogen derived from water moisture in the coal matrix. The $\delta^{2}H$ values of thermogenic hydrocarbons are also controlled by the paleohydrology of vegetation and hydrogen exchange with pore water during maturation in the sedimentary basin. The evaluation of the maturity level of hydrocarbon gases based on their hydrogen isotopic composition demands caution.

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[Table Captions]

Table 1. Vitrinite reflectance, elemental compositions, and H/C and O/C atomic ratios of Eocene Yubari coal and artificially matured coal (AMC #1 to #5) pyrolyzed at 330–390°C for 72 h under an anhydrous closed system.

Table 2. Independent and cumulative yields of gases generated from Eocene Yubari coal pyrolyzed under a semi-open system.

Table 3. Yields of gases generated from Eocene Yubari coal pyrolyzed under an anhydrous closed system.

Table 4. Stable carbon and hydrogen isotopic compositions of gases generated from Eocene Yubari coal pyrolyzed under a semi-open system.

Table 5. Stable carbon and hydrogen isotopic compositions of gases generated from Eocene Yubari coal pyrolyzed under a closed system. The apparent isotopic composition for the increased differential gas fraction was determined from the

mass balance of the gases.

[Figure Captions]

Fig. 1. Typical pulsed discharge helium ionization detector (PDHID) chromatograms of gas components generated from Eocene Yubari coal samples pyrolyzed at (a) 330°C, (b) 340°C, and (c) 370°C for 72 h. VR_r is the vitrinite reflectance of pyrolyzed coal.

Fig. 2. Changes in the yield of gas components with increasing VR_r under the semi-open and closed system pyrolysis of Eocene Yubari coal. The cumulative yield of the gas components in the semi-open system pyrolysis and the independent yield of gas components in the closed system pyrolysis are plotted.

Fig. 3. Changes in the $\delta^{13}C$ values of methane, ethane, and propane expelled from Eocene Yubari coal with increasing VR_r under semi-open and semi-closed systems. The $\delta^{13}C$ values of the hydrocarbon gases in the semi-open system are measured values, while those in the semi-closed system are the calculated values for the increase in the differential gas fraction between two successive pyrolysis

experiments. The VR_r in the semi-open system is the logarithmic mean value of two successive pyrolysis experiments, while that in the semi-closed system is the measured value.

Fig. 4. Changes in the δ^2H values of methane, ethane, and propane expelled from Eocene Yubari coal with increasing VR_r under semi-open and semi-closed systems. The δ^2H values of the hydrocarbon gases in the semi-open system are measured values, while those in the semi-closed system are the calculated values for the increase in the differential gas fraction between two successive pyrolysis experiments. The VR_r in the semi-open system is the logarithmic mean value of two successive pyrolysis experiments, while that in the semi-closed system is the measured value.

Fig. 5. The paths of evolution of the δ^{13}C values of methane, ethane, and propane expelled from Eocene Yubari coal with increasing VR_r under semi-open and semi-closed systems. (a) Relationship between the δ^{13}C values of methane and ethane. (b) Relationship between the δ^{13}C values of ethane and propane.

Table 1. Vitrinite reflectance, elemental compositions, and H/C and O/C atomic ratios of Eocene Yubari coal and artificially matured coal (AMC #1 to #5) pyrolyzed at 330–390°C for 72 h under an anhydrous closed system.

Sample or Pyrolysis No.	Temp. (ºC)	Time (h)	VR_r (%)	C	H	O* (%)	N	S	Atomic H/C	Atomic O/C
Original Coal			0.46	77.8	6.31	14.5	1.28	0.14	0.97	0.14
AMC #1	330	72	0.60	82.9	5.87	9.4	1.67	0.18	0.85	0.09
AMC #2	340	72	0.97	81.4	5.10	11.6	1.80	0.17	0.75	0.11
AMC #3	350	72	1.29	85.5	5.32	7.2	1.79	0.20	0.75	0.06
AMC #4	370	72	1.46	87.4	4.66	5.7	2.00	0.19	0.64	0.05
AMC #5	390	72	1.70	87.4	4.49	5.9	2.01	0.15	0.62	0.05

*: by difference (dry ash free)

Table 2. Independent and cumulative yields of gases generated from Eocene Yubari coal pyrolyzed under a semi-open system.

Pyrolysis No.	Temp. (ºC)	Time (h)	VR_r* (%)	Yield of Gases (μL/gCoal)									
				H_2	CO	C_1	CO_2	C_2H_4	C_2	C_3H_6	C_3	*i*-C_4	*n*-C_4
Original Coal			0.46	Independent Yield									
#1	330	72	0.60	375	1206	1721	2115	15	525	54	529	143	184
#2	340	72	0.97	391	229	1023	282	15	374	55	318	71	102
#3	350	72	1.29	513	151	955	114	13	382	46	288	67	123
#4	370	72	1.46	892	180	1467	194	13	535	37	388	70	178
#5	390	72	1.70	1321	202	2465	389	11	741	24	464	82	213
Original Coal			0.46	Cumulative Yield									
#1CY	330	72	0.60	375	1206	1721	2115	15	525	54	529	143	184
#2CY	340	72	0.97	766	1435	2745	2397	30	899	110	847	214	285
#3CY	350	72	1.29	1279	1587	3700	2511	42	1281	156	1135	281	408
#4CY	370	72	1.46	2171	1767	5167	2705	55	1816	193	1523	351	586
#5CY	390	72	1.70	3492	1969	7632	3094	66	2557	217	1987	434	799

*: VR_r value from corresponding closed system pyrolysis shown in Table 1.

Table 3. Yields of gases generated from Eocene Yubari coal pyrolyzed under an anhydrous closed system.

Pyrolysis No.	Temp. (ºC)	Time (h)	VR_r (%)	Yield of Gases (μL/gCoal)									
				H_2	CO	C_1	CO_2	C_2H_4	C_2	C_3H_6	C_3	*i*-C_4	*n*-C_4
				Independent Yield									
#1	325	24	0.53	191	817	713	878	11	189	44	192	40	52
#2	330	72	0.60	411	739	1395	877	13	410	43	389	99	135
#3	350	48	1.03	1011	1269	2631	1572	25	961	85	890	250	436
#4	350	72	1.29	1279	1040	3033	1123	26	1060	92	1020	270	531
#5	370	72	1.46	2409	1367	5383	1849	43	1925	135	1593	421	926
#6	390	72	1.70	3103	1523	8798	2530	57	3055	179	2337	581	1341
#7	390	168	1.80	2772	1647	11677	2802	70	3575	225	2855	789	1779
				Differential Yield									
#1D	325	24	0.53	191	817	713	878	11	189	44	192	40	52
#2D	330	72	0.60	220	-78	682	-2	2	221	-1	197	60	83
#3D	350	48	1.03	601	530	1236	695	12	552	41	501	150	301
#4D	350	72	1.29	268	-229	402	-449	0	98	8	130	20	95
#5D	370	72	1.46	1130	326	2350	726	17	866	43	572	151	395
#6D	390	72	1.70	694	156	3414	680	14	1130	44	744	160	415
#7D	390	168	1.80	-331	124	2879	273	13	520	47	518	208	438

Table 4. Stable carbon and hydrogen isotopic compositions of gases generated from Eocene Yubari coal pyrolyzed under a semi-open system.

Sample or Pyrolysis No.	Temp. (°C)	Time (h)	VR_r (%)	VR_{mean}* (%)	$\delta^{13}C$ (‰)				$\delta^{2}H$(‰)		
					C_1	C_2	C_3	CO_2	C_1	C_2	C_3
Original Coal			0.46								
#1	330	72	0.60	0.53	-35.9	-28.9	-26.9	-26.4	-306	-252	-207
#2	340	72	0.97	0.76	-37.3	-28.2	-25.9	-24.3	-298	-253	-229
#3	350	72	1.29	1.12	-36.9	-27.7	-25.6	-22.5	-290	-248	-229
#4	370	72	1.46	1.37	-35.7	-26.4	-24.6	-21.5	-279	-241	-214
#5	390	72	1.70	1.58	-31.0	-23.4	-21.6	-19.5	-262	-225	-189

*: Logarithmic mean of VR_r values from two successive pyrolysis experiments.

Table 5. Stable carbon and hydrogen isotopic compositions of gases generated from Eocene Yubari coal pyrolyzed under a closed system. The apparent isotopic composition for the increased differential gas fraction was determined from the mass balance of the gases.

Pyrolysis No.	Temp. (ºC)	Time (h)	VR_r (%)	$\delta^{13}C_1$ (‰)	$\delta^{13}C_2$ (‰)	$\delta^{13}C_3$ (‰)	$\delta^{2}H_{C1}$ (‰)	$\delta^{2}H_{C2}$ (‰)	$\delta^{2}H_{C3}$ (‰)
				Measured values			Measured values		
#1	325	24	0.53	-34.8	-29.5	-26.8	-337	-267	-278
#2	330	72	0.60	-35.8	-29.8	-26.4	-325	-266	-233
#3	350	48	1.03	-36.7	-29.4	-26.6	-325	-282	-275
#4	350	72	1.29	-38.1	-29.7	-26.5	-313	-261	-241
#5	370	72	1.46	-37.9	-29.0	-26.7	-297	-254	-230
#6	390	72	1.70	-35.9	-28.3	-26.6	-291	-245	-222
#7	390	168	1.80	-34.3	-27.6	-25.5	-257	-229	-205
				Apparent values*			Apparent values*		
#1CA	325	24	0.53	-34.8	-29.5	-26.6	-331	-266	-258
#2CA	330	72	0.60	-35.7	-29.8	-26.7	-332	-270	-261
#3CA	350	48	1.03	-38.0	-29.8	-26.8	-325	-275	-258
#4CA	350	72	1.29	-37.8	-29.0	-26.4	-297	-258	-235
#5CA	370	72	1.46	-35.8	-27.9	-26.0	-267	-234	-208
#6CA	390	72	1.70	-32.4	-26.3	-25.3	-228	-200	-171
#7CA	390	168	1.80	-28.8	-24.8	-24.6	-191	-166	-136

*: Calculated value for differential gas fraction.

Fig. 1

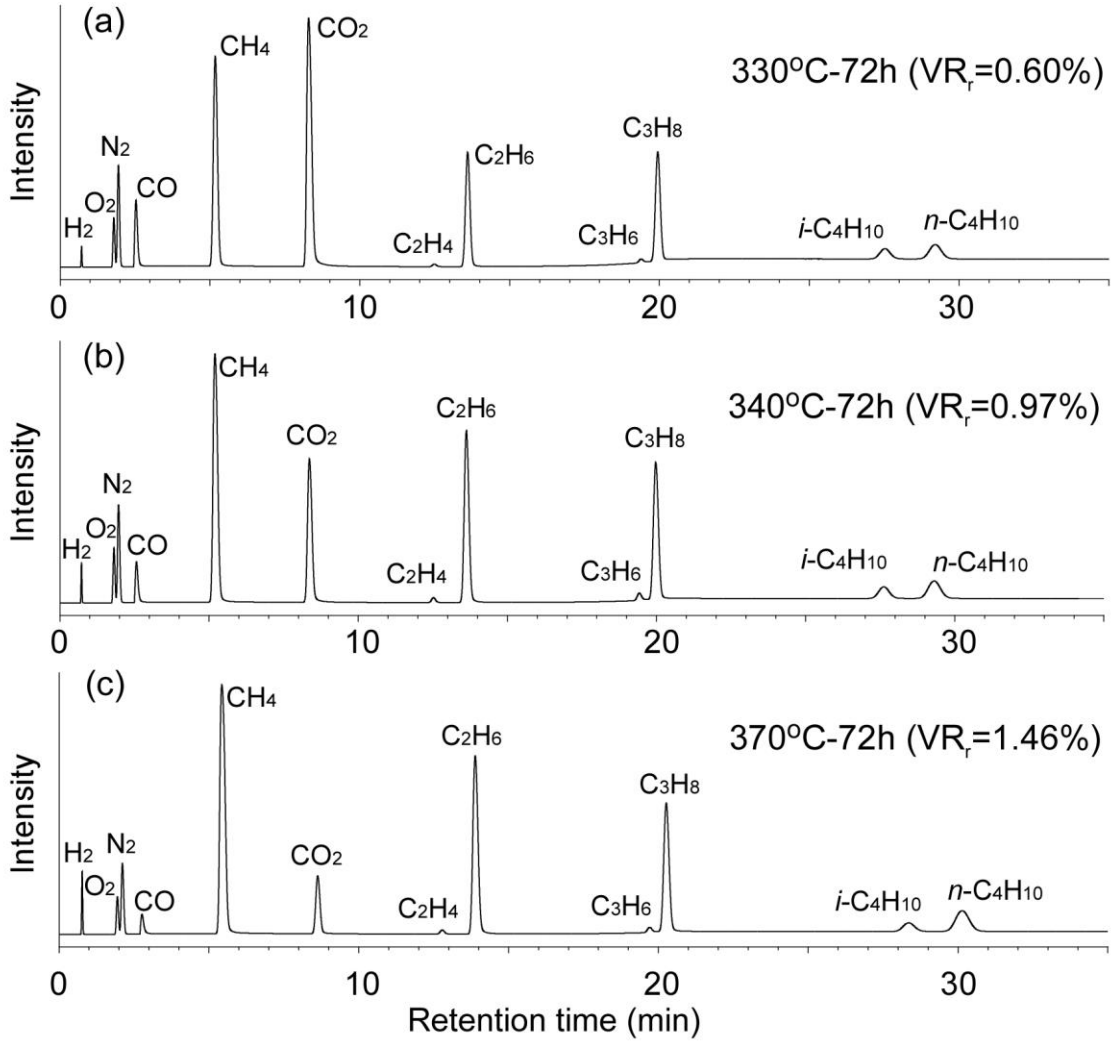

(a)
330°C-72h (VR$_r$=0.60%)
(b)
340°C-72h (VR$_r$=0.97%)
(c)
370°C-72h (VR$_r$=1.46%)
Intensity
H$_2$
O$_2$
N$_2$
CO
CH$_4$
CO$_2$
C$_2$H$_4$
C$_2$H$_6$
C$_3$H$_6$
C$_3$H$_8$
i-C$_4$H$_{10}$
n-C$_4$H$_{10}$
0
10
20
30
Retention time (min)

Fig. 2

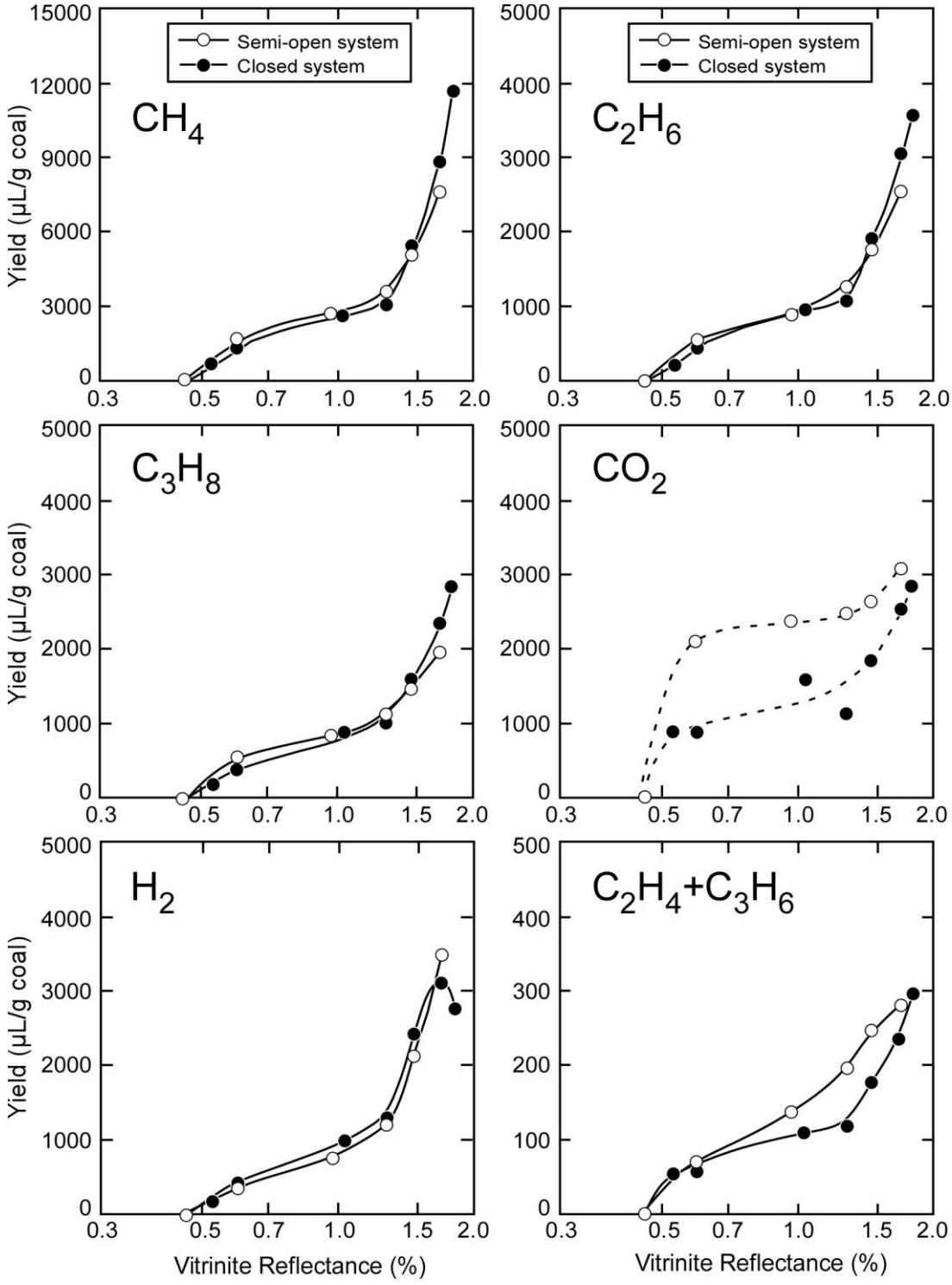

Semi-open system
Closed system
CH4
C2H6
C3H8
CO2
H2
C2H4+C3H6
Yield (μL/g coal)
Vitrinite Reflectance (%)

Fig. 3

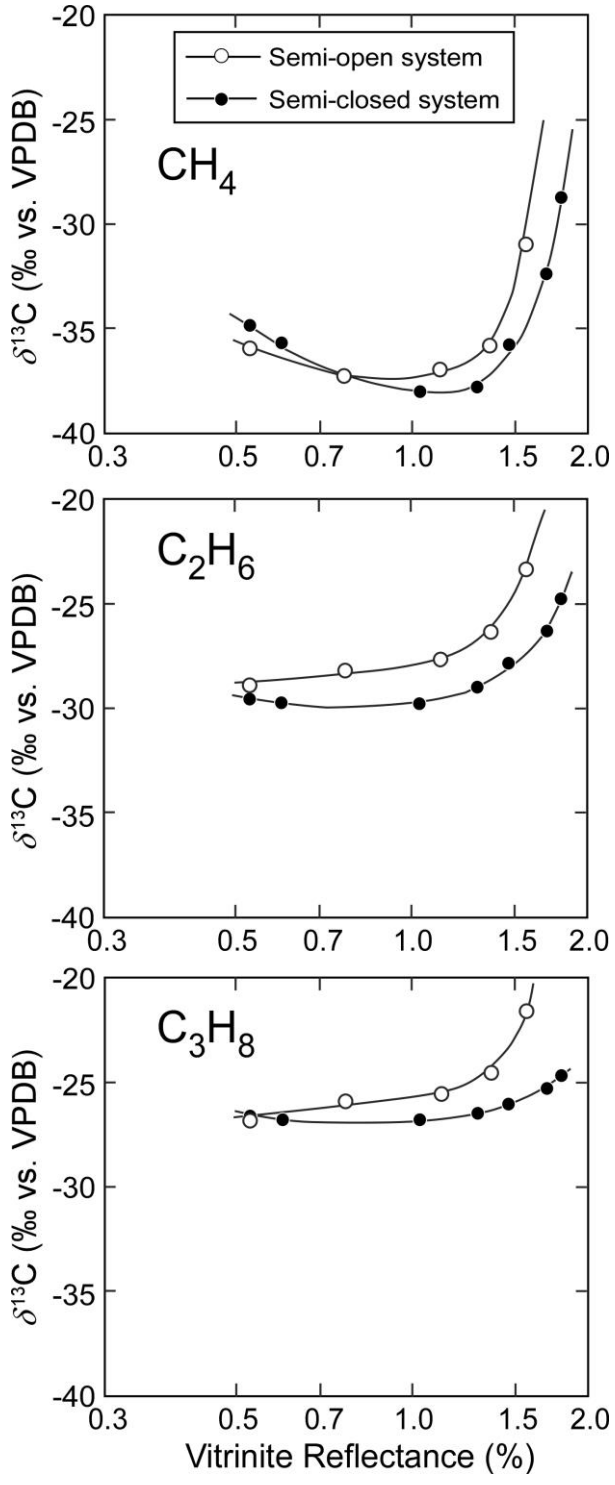
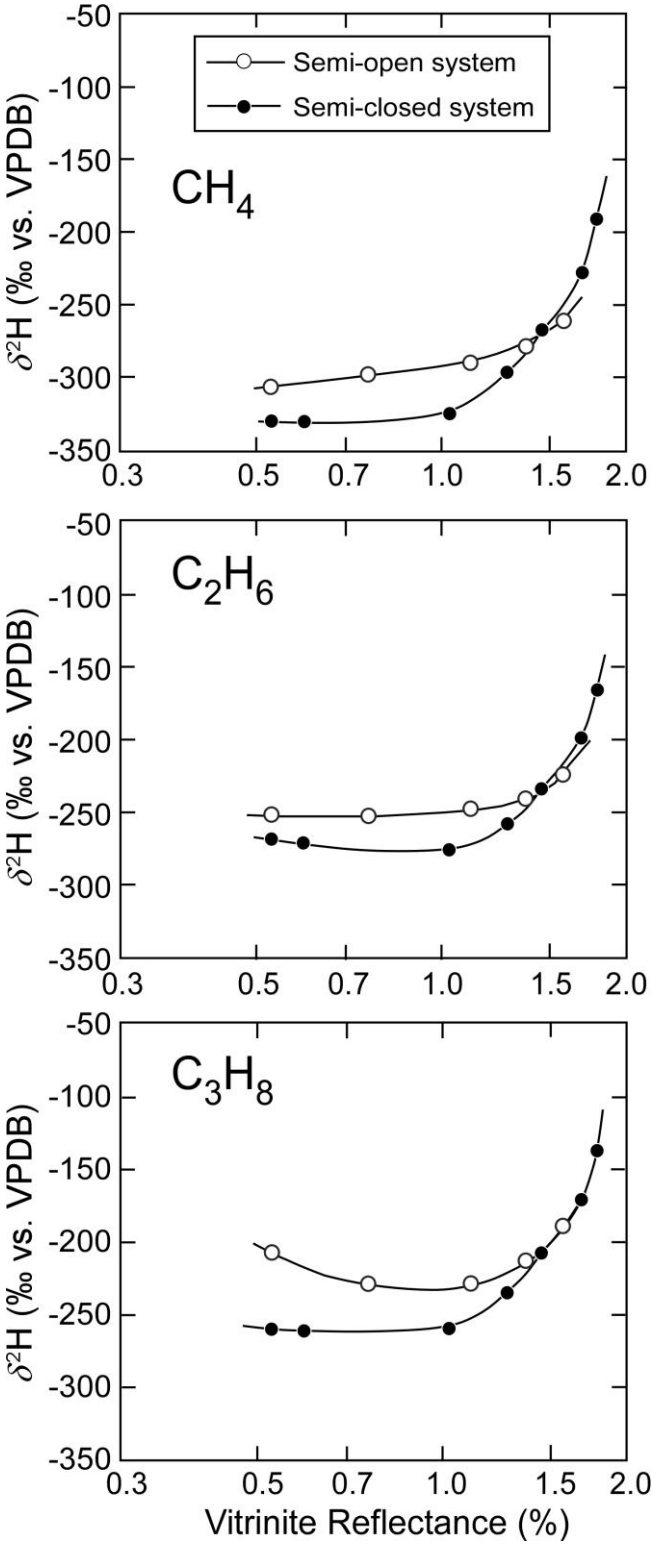
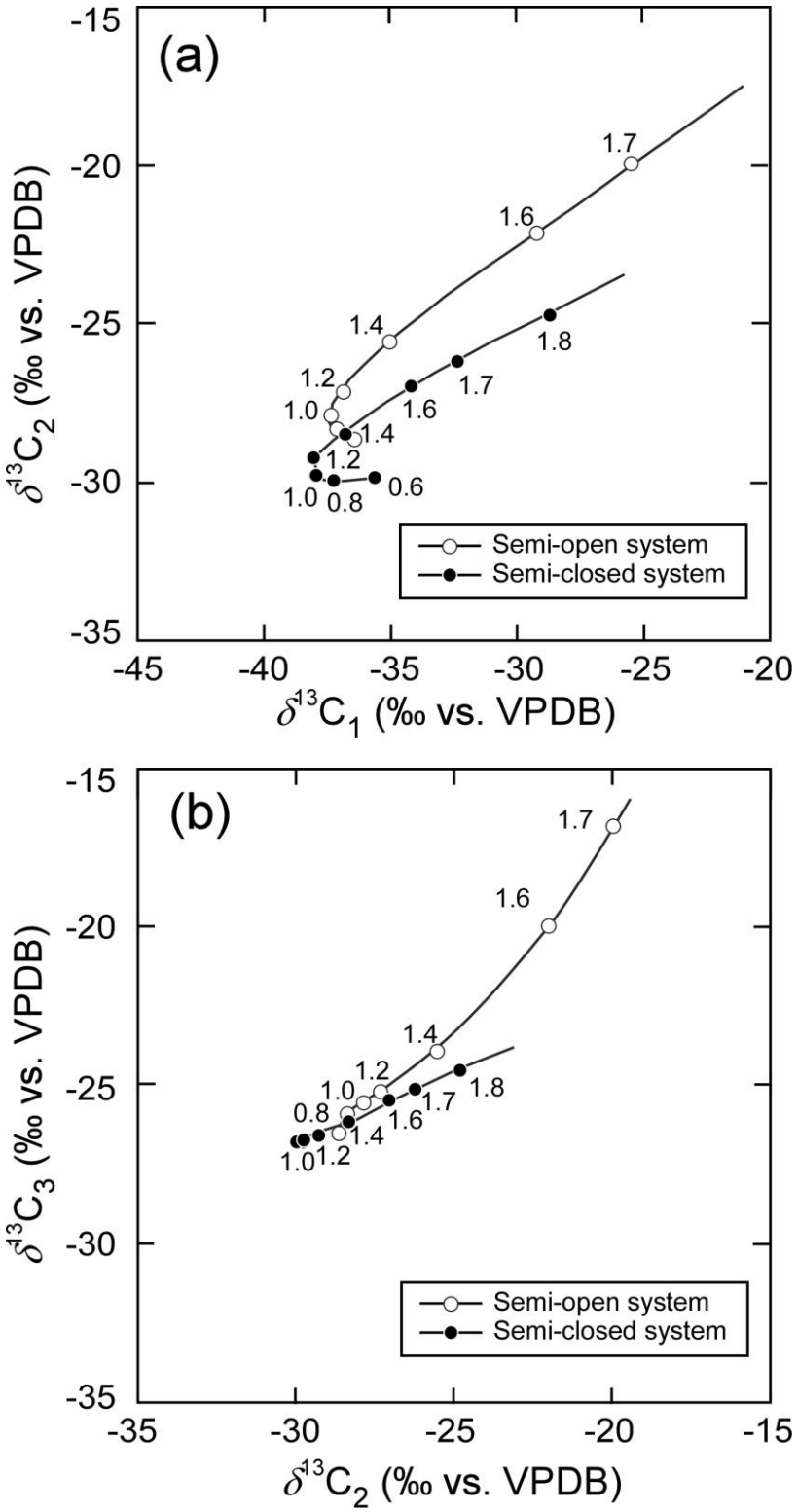

Semi-open system
Semi-closed system
CH4
C2H6
C3H8
δ13C (‰ vs. VPDB)
-20
-25
-30
-35
-40
0.3
0.5
0.7
1.0
1.5
2.0
Vitrinite Reflectance (%)

Fig. 4


Semi-open system
Semi-closed system
CH4
C2H6
C3H8
δ2H (‰ vs. VPDB)
-50
-100
-150
-200
-250
-300
-350
0.3
0.5
0.7
1.0
1.5
2.0
Vitrinite Reflectance (%)

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(a)
-15
-20
-25
-30
-35
-45
-40
-35
-30
-25
-20
$\delta^{13}C_2$ (‰ vs. VPDB)
$\delta^{13}C_1$ (‰ vs. VPDB)
1.7
1.6
1.4
1.2
1.0
1.8
1.7
1.6
1.4
1.2
1.0
0.8
0.6
Semi-open system
Semi-closed system
(b)
-15
-20
-25
-30
-35
-35
-30
-25
-20
-15
$\delta^{13}C_3$ (‰ vs. VPDB)
$\delta^{13}C_2$ (‰ vs. VPDB)
1.7
1.6
1.4
1.2
1.0
0.8
1.8
1.7
1.6
1.4
1.2
1.0
Semi-open system
Semi-closed system

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