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Hydrogen Gas of Organic Origin in Shales and Metapelites

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Abstract

The changes in inorganic and organic gases retained in shales and metapelites with increasing heating temperature are not fully understood. The compositional and isotopic changes of residual gases such as H$_2$, CH$_4$, and CO$_2$ in marine shales and metapelites during burial diagenesis and metamorphism were investigated in the present study. Shale rocks and metapelites which experienced paleo-temperatures in the range of 100 to 600ºC were collected from the borehole cores in Niigata sedimentary basin and outcrops exposed in Kochi district, Japan. Gases released from shale or metapelite fragments during pulverization in the laboratory were analyzed as the residual gas.

The major residual gas in shales and metapelites changes from CO$_2$, CH$_4$, to H$_2$ in this order with increasing temperature. Drastic decrease of CO$_2$ derived from decarboxylation of sedimentary organic matter is due to the expulsion of pore fluids with dissolved CO$_2$. The CH$_4$ concentration in residual gas subsequently increases with organic maturation and reaches the maximum at paleo-temperature of ca. 250ºC. The CH$_4$ concentration decreases during late metagenesis to metamorphism probably due to the formation of H$_2$ gas and graphite. The H$_2$ starts to increase at paleo-temperature of ca. 200ºC. The H$_2$ gas is the most abundant gas in residual gas of metapelite. The $\delta^2$H value of H$_2$ in shales and metapelites is quite low to be in the range of ca. –850 to –650‰. The change of major residual gas from CH$_4$ to H$_2$ with increasing paleo-temperature and the significantly low $\delta^2$H values of H$_2$ suggest that H$_2$ gas in shales and metapelites is largely derived from liberation of hydrogen in organic matter.
1. Introduction

In connection with shale gas exploration, the influence of maceral composition, thermal maturation, mineral type, and moisture on methane sorption have been comparatively well studied, as has the gas storage capacity of shale (e.g. Ross and Bustin, 2009; Slatt and O’Brien, 2011; Curtis et al., 2012; Milliken et al., 2013; Gasparik et al., 2014). However, the concentrations and changes in the proportional composition of components such as CO₂, CH₄, and H₂ in the gas retained in shale rocks with increasing maturation are not well understood. In particular, our knowledge regarding H₂ in shale and metapelites is poor.

Hydrogen gas seeps have been reported in numerous localities, but are most commonly related to the serpentinization of mafic to ultramafic rocks, geothermal alteration, tectonic fault activity, and/or deep gas seeps. The H₂ gas in these gas seeps is characteristically depleted in deuterium (²H). For example, ²H-depleted H₂, with a hydrogen isotope ratio (δ²H) of less than −500‰, has been found in H₂-rich gases associated with the serpentinization of ophiolite (Neal and Stanger, 1983), deep gases (Jefferey and Kaplan, 1988), gases from geothermal areas (Mayhew et al., 2013), and fault gases (Sugisaki et al., 1983; Randolph et al., 1985). This ²H-depleted H₂ is thought to be generated physically by water-rock interactions forming the silanol function or chemically by the reduction and dissociation of H₂O (Saruwatari et al., 2004; Mayhew et al., 2013). Laboratory open-system pyrolysis experiments on shales and coals have been recently performed to show the liberation of molecular H₂ from sedimentary organic matter (Li et al., 2015). Sedimentary organic matter can be another important source of H₂ in the Earth’s crust, although there are few reports of
natural H₂ derived from the dissociation of carbon-hydrogen bonds in sedimentary organic matter.

In this study, we investigated the concentrations and changes in the proportional composition of components, such as CO₂, CH₄, and H₂, in the gases released during the pulverization of shales and metapelites at different levels of thermal maturation and metamorphism. The carbon and hydrogen isotopic compositions of CH₄ and H₂ in shale rocks and metapelites were also determined to enable an understanding of the genetic interrelationships among gas components. A knowledge of the changes in the composition of gases in shale rocks and metapelites during burial diagenesis and metamorphism would also enable a better understanding of the behavior of gases released from shale rocks in association with their destruction and deformation in the deep subsurface.

2. Materials and Methods

2.1 Shale and Metapelite Samples

Shale rocks and metapelites that had experienced a paleo-temperature in the range of 100 to 600°C were collected from the borehole cores of MITI-Mishima, drilled in Niigata Prefecture, and outcrops exposed in the Shimanto and Chichibu belts, the Mikabu greenstone belt, and the Sanbagawa metamorphic belt in the Kochi district (Fig. 1). The MITI-Mishima borehole was drilled by the Japanese Ministry of International Trade and Industry (METI) in Niigata Prefecture between 1991 and 1992. The MITI-Mishima borehole penetrated the Pleistocene Uonuma Formation to the Middle Miocene Upper Nanatani Formation. The maximum drilling depth of the
MITI-Mishima borehole is 6300 m and its bottom-hole temperature is 226°C. The available downhole petrophysical log data, paleontological data, and petroleum geochemical data, along with the results of seismic profiles, have been summarised by the Japan National Oil Corporation (presently the Japan Oil, Gas, and Metals National Corporation) (JNOC, 1992). Changes in shale porosity, vitrinite reflectance, cuttings gas composition, and various maturity parameters have been analyzed by JNOC (1992), Okubo (1998), and Suzuki et al. (2013) (Fig. 2). The Sanbagawa metamorphic belt is divided into Ooboke Nappe and Besshi Nappe based on lithology and metamorphic age (Takasu and Dallmeyer, 1990). The geologic age of the protoliths of the Sanbagawa metamorphic belt is Triassic to Jurassic, and the metamorphism of these rocks proceeded during the Late Cretaceous. The metapelite samples were collected from outcrops of Besshi Nappe exposed along the Asemi-gawa River, where metamorphic rocks of the chlorite, garnet, albite-biotite, and oligoclase-biotite zones are distributed (Banno, 1998). The metamorphic temperature of metapelites increases gradually from the chlorite zone (300°C) to the oligoclase-biotite zone (610°C) (Banno and Sakai, 1989).

The Mikabu greenstone belt is distributed lenticularly between the Sanbagawa metamorphic belt and the Chichibu belt, comprising greenstone, shale, limestone, and chert. Carboniferous and Late Triassic conodont fossils have been found in the Mikabu greenstone belt. Sedimentary rocks in the Mikabu greenstone belt have experienced weak metamorphism, and belong to the chlorite and pumpellyite-actinolite zones (Banno, 1998).

The Chichibu belt is a Jurassic to Early Cretaceous accretionary prism comprising chert, greenstone, and shale. The Chichibu belt is divided by a large fault
into northern and southern units. The northern unit is mainly composed of chert, greenstone, and phyllite, with some sandstone, limestone, and dolomite. The southern unit is mainly composed of chert, greenstone, sandstone, and conglomeratic shale with some limestone, alternation of sandstone and shale, felsic pyroclastics, siliceous shale, and black shale.

The Shimanto belt is widely distributed in southeastern Japan, extending from the Nansei Islands through Kyushu, Shikoku, the Kii Peninsula, Akaishi, and the Kanto Mountains to the Boso Peninsula. The Shimanto belt of Shikoku is divided by the Aki Tectonic Line into a northern and a southern belt. The northern belt is composed of the Lower Cretaceous Shinjogawa and the Upper Cretaceous Aki groups (Fig. 1). The Aki group is mainly composed of an alternation of sandstone and shale. A blocky olistolith comprising deformed basaltic rocks, layered chert, shale, and sandstone is often intercalated in the gray to black shale matrix. The southern belt is composed of the Eocene to the Lower Oligocene Muroto Peninsula and the Upper Oligocene to the Lower Miocene Nabae groups (Fig. 1). The southern belt mainly comprises an alternation of shale and sandstone, and a subduction complex melange, remarkably deformed with many slump structures. Shale samples were collected from outcrops of Aki, the Muroto Peninsula and the Nabae groups distributed along the eastern coast of Tosa Bay.

All the shale and metamorphic rocks from MITI-Mishima borehole and Kochi district were deposited in the marine environment with a variable contribution of terrestrial organic matter. According to previous studies of organic matter in Miocene shales from MITI-Mishima (JNOC, 1992; Suzuki et al., 2013) and Paleogene to Cretaceous shales from the Shimanto belt (Maki et al., 1980), the shale rock
samples used in this study consists of Type II and II/III kerogens. The depositional environment of metapelites in the Sanbagawa belt has not been well studied. The formation of these metapelites under low temperatures and high pressure metamorphism due to accretion tectonics similar to those of the marine shales in the Shimanto belt suggests that the kerogen material within metapelites from Kochi district are also Type II to II/III kerogens. There may be some differences in the organic type among the samples, but this would not have much influence on the geochemical characteristics of kerogen at the highly mature stage.

2.2 Pulverization and Residual Gas Recovery

Residual gas in shales and shaley layers is present as sorbed gas on an organic and inorganic matrix, free gas in various pore spaces, and dissolved gas in pore water. These residual gases can be classified methodologically into residual free gas and residual adsorbed gas. Gas released from shale fragments during pulverization is defined as residual free gas. The pulverization of the shale fragments was conducted using a P-6 planetary ball mill and an alumina mill pot, with needle valves and a sampling port (Fritsch GmbH, Idar-Oberstein, Germany). The inner volume of the mill pot was 80 cm\(^3\). Shale or pelitic rock fragments in the size range of ca. 5–7 mm were pulverized in the alumina mill pot under a helium atmosphere. Gas was sampled with a gastight syringe directly from the sampling port of the alumina mill pot and analyzed as residual free gas.

A preliminary study of the relationship between pulverization time and gas recovery has shown that the recovery of hydrocarbon gases and molecular hydrogen is almost complete after 20 min of pulverization at a spinning rate of 300 rpm (Suzuki et
al., 2013). However, the concentration of CO$_2$ in residual gas initially increases, but then tends to decrease with increased pulverization time, suggesting the adsorption of CO$_2$ on mineral surfaces during pulverization. Therefore, the concentration of CO$_2$ in the residual free gas was underestimated. The concentration of CO$_2$ is generally highest in the residual gas obtained after 20 to 40 min of pulverization. In this study, gas released from rock fragments (5–7 mm) during pulverization for 30 min in the alumina mill pot under a helium atmosphere was analyzed as residual free gas. The temperature of the alumina mill pot during pulverization was less than 45ºC. After pulverization by the ball mill, the grain size of the rock powder was measured by a laser diffraction-scattering method using a grain-size analyzer (LA-920: Horiba, Kyoto, Japan) and was determined to generally be in the range of 3–7 µm.

2.3 Kerogen isolation and elemental analysis

The pulverized shale or metapelite was extracted by Soxhlet extraction method with benzene and methanol (9:1) solvent for 2 days. The solvent extraction residue was demineralized with 6 N HCl/47% HF (1:1, 2 days at 60 ºC) and then washed with distilled water to pH 7. Isolated kerogen was centrifuged and dried. Kerogen was extracted again with the same solvent by ultrasonication before the elemental analysis. Total organic carbon (TOC), total nitrogen and total hydrogen contents were determined using an EA 3000 elemental analyzer (Euro Vector Co., Milan, Italy) or a MT-3 organic micro elemental analyzer (Yanaco Technical Sci. Co., Tokyo, Japan). The pulverized shale or metapelite was weighed and placed in a silver capsule or a platinum sample boat with drops of 1N HCl to remove carbonates. The carbonate-free sample and isolated kerogen were dried at 120ºC for 2 h and analyzed
by the elemental analyzer. Vitrinite separation was made on the 2 to 4 mm rock fragments by the demineralization with 6 N HCl/47% HF (1:1, 2 days at 60ºC). Vitrinite was concentrated by the float and sink method using CCl₄. The mean vitrinite reflectance (VR₀) of randomly-oriented vitrinite grains was measured in the Research Center of Teikoku Oil Co. Ltd. (INPEX Co. Ltd. at present).

2.4 Residual Gas Analysis

The composition of the residual gas in the rock fragments was measured by gas chromatography (GC) using an instrument (7890A: Agilent, Santa Clara, CA, 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., Nagoya, Japan). The oven temperature of the GC was programmed to 40ºC for 3 min, increased to 300ºC at a rate of 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 or 50 µL sampling loop. Compounds were identified by comparing the retention times with those of reference standards in a gas mixture containing CH₄, C₂H₄, C₂H₆, C₃H₆, C₃H₈, i-C₄H₁₀, n-C₄H₁₀, H₂, CO, and CO₂. The detailed analytical procedure is described in Saito et al. (2012).

2.5 Isotope Analysis

According to Takahashi et al. (2014), stable carbon isotopic analysis was performed by GC-combustion-isotope ratio mass spectrometry (GC-C-IRMS: 6890A (Agilent) and MAT 252 (Thermo Scientific Finnigan, Waltham, MA, USA)) 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 increased to 300ºC at a rate of 15ºC/min, and finally held at 300ºC for 20 min. 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, Delta V Advantage, Thermo Scientific) using the same micropacked column and He as the carrier gas. The oven temperature program was identical to that used for the GC-C-IRMS analysis. The thermal conversion furnace between the GC and IRMS was maintained at 1450ºC. Stable carbon and hydrogen isotope data were reported as $\delta^{13}$C and $\delta^2$H values relative to the Vienna Pee Dee Belemnite (VPDB) and Vienna Standard Mean Ocean Water (VSMOW) scales. The $\delta^{13}$C and $\delta^2$H values were determined by comparison with the MZ3-01 CH$_4$ standard ($\delta^{13}$C of –31.1‰; SI Science Co., Saitama, Japan) and the Indiana CH$_4$ #1 standard ($\delta^{13}$C of –38.25‰ and $\delta^2$H of –160.8‰; Indiana Univ., Bloomington, IN, USA), respectively. The $\delta^{13}$C value of the MZ3-01 CH$_4$ standard has been calibrated against NBS 19, and the $\delta^{13}$C and $\delta^2$H values of the Indiana CH$_4$ #1 standard are normalized to NBS 19/L-SVEC and SLAP, respectively. The H$_3^+$ factor of the mass spectrometer was determined once each day using external reference gas injections and was consistently < 10 ppm. The selected gas samples were measured repeatedly, four to five times, to determine the $\delta^{13}$C and $\delta^2$H values. The results showed that the analytical precision of the $\delta^{13}$C and $\delta^2$H values was at most ± 0.46‰ and ± 7‰, respectively. The $\delta^{13}$C values of kerogen or carbonaceous material were analyzed using an elemental analyzer-isotope ratio mass spectrometry (EA1112-Delta V Advantage ConFlo IV system, Thermo Scientific) at SI Science Co. Ltd., Japan.
2.6 Maximum Heating Temperature

The paleo-maximum temperature of the shale rocks and metapelites was estimated by VR\textsubscript{o}, metamorphic mineral assemblages, and degree of graphitization. The paleo-maximum temperature of shale rocks from the MITI-Mishima borehole and the Kochi district was estimated by SIMPLE-R\textsubscript{o} (Suzuki et al., 1993) using VR\textsubscript{o} values in the range of 0.4 to 3.5%. Taking into account the sediment accumulation (c.a. 2000 m) during the last 1.8 m.y. (million years) and the present-day geothermal gradient of 3.36ºC/100 m, the rate of temperature increase used to estimate the paleo-maximum temperature of shale rocks from the MITI-Mishima borehole was assumed to be 40ºC/m.y. (million years). Temperatures estimated by SIMPLE- R\textsubscript{o} were almost the same as the bottom-hole temperatures, showing that the present temperature of the MITI-Mishima borehole is almost the same as the maximum heating temperature (Table 1). The rate of temperature increase of shale rocks from the Kochi district was assumed to be 5ºC/m.y. by considering the present-day geothermal gradient, which ranges from 2 to 3ºC/100 m (Toriumi and Teruya, 1988; Ashi and Taira, 1993), and accretion tectonics (Sakaguchi, 1996; Hara and Kimura, 2008) (Table 2). The Sanbagawa metamorphic belt includes prehnite-pumpellyite, chlorite, garnet, biotite, and oligoclase biotite zones (Banno et al., 1978; Enami, 1983). The metamorphic temperature estimated based on these mineral assemblages ranges from c.a. 250 to 600ºC, and increases continuously from south to north (Banno et al., 1978; Enami, 1983; Banno and Sakai, 1989) (Table 2 and Fig. 1).
3. Results

3.1 Organic Matter Type and Thermal Alteration

Total organic carbon (TOC) concentrations of shale rocks from MITI-Mishima borehole and Kochi district are in the ranges of 0.62 to 1.65% and 0.17 to 0.91%, respectively (Tables 1 and 2). Metapelites from the Sanbagawa metamorphic belt showed a relatively low TOC concentration in the range of 0.07 to 0.76% (Table 2). VR₀ value of the sediment samples from MITI-Mishima borehole generally increases with depth and reaches 0.5% at about 2500m depth (Fig. 2). However, VR₀ values in the depth between 3000 to 4500m are scattered in the range of 0.4 to 0.8%. VR₀ values reaches 1.0% and 2.0% at about 5000m and 6000m, respectively. The relative abundance of C₂ to C₅₊ hydrocarbons increases at about 3300m (VR₀ = 0.6 to 0.7%), suggesting the top of the oil generation zone (Fig. 2). Cuttings gas in the deepest part is mainly composed of C₁ without any traces of C₂ to C₅₊ hydrocarbons, showing that the deepest part of borehole is in the dry gas zone. Porosity of mudstones at 5000m (VR₀=c.a. 1.0%) and 6000m (VR₀=c.a. 2.0%) are reported to be c.a. 5% and c.a. 2%, respectively (JNOC, 1992) (Fig. 2). Shale rocks from Shimanto belt have VR₀ values in the range of 1.0 to 2.7%, being mostly in the wet to dry gas zone. VR₀ values of shale rocks from Chichibu belt are generally more than 3.0%. Carbonaceous material in the samples from Mikabu greenstone and Sanbagawa metamorphic belts showed anisotropy in VR₀ values. The anisotropy in VR₀ is thought to be related to the graphitization of carbonaceous material during metamorphism. VR₀ values were not determined for the samples from Mikabu greenstone and Sanbagawa metamorphic belts.
The atomic H/C ratio of kerogen material in shales and metamorphic rocks from the Kochi district showed a significant decrease in hydrogen concentration with increasing paleo-maximum temperature (Fig. 3), suggesting that graphitization was progressing. X-ray diffraction analysis have been performed on carbonaceous material in selected samples from the Sanbagawa metamorphic belt (Suzuki et al., 2013). The spacing of the 002 plane (d002) of disordered graphite decreased from 3.45 to 3.39 (Å) as metamorphic temperatures increased from 400 to 600ºC. In the same temperature range, the half-width of the graphite 002 peak also decreased drastically, indicating an increase in graphite crystallinity. The significant graphitization at metamorphic temperatures from 400 to 600 ºC corresponds to the change of the atomic H/C from 0.2 to 0.1. The graphitization observed in the samples was consistent with that reported in previous studies of the graphitization of carbonaceous material in the Sanbagawa metamorphic belt (Itaya, 1981).

The $\delta^{13}$C$_{\text{bulk}}$ values ($\delta^{13}$C value of kerogen or bulk carbonaceous material) of some selected shale rocks at higher maturity level and metapelites were measured to be in the range of ca. $\sim$27 to $\sim$21‰ (Table 2). The $\delta^{13}$C$_{\text{bulk}}$ values of shale rocks from Chichibu Belt are lower compared to those of metapelites from Mikabu Greenstone and Sanbagawa Metamorphic Belts. The $\delta^{13}$C$_{\text{bulk}}$ values of metapelite increased with increasing metamorphic grade from chlorite zone to biotite-albite zone, which is consistent with the results of previous studies (Hoefs and Frey, 1976; Morikiyo, 1986).

3.2 Compositional Change in Residual Gas

The concentrations of CH$_4$, C$_2$H$_6$, CO$_2$, and H$_2$ in the residual gas in shales and metapelites from MITI-Mishima and Kochi district are normalized against the
TOC concentration (Tables 1 and 2). The concentration changes of these gases with increasing paleo-temperature are shown in Fig. 4. The concentration of CH$_4$ in the residual gas from shale rocks tended to increase with increasing paleo-temperature and reached its highest concentration of 1500 to 1700 μL/gTOC at paleo-temperatures around 200 to 250°C (Fig. 4). The concentration of CH$_4$ in the residual gas from metapelites, which attained paleo-temperatures of more than 300°C, was comparatively lower (less than 800 μL/gTOC). CH$_4$ concentration decreased in the temperature range of 250 to 600°C. The concentration of C$_2$H$_6$ was generally less than 110 μL/gTOC. The highest concentration of C$_2$H$_6$ was observed in rocks at assumed paleo-temperatures of around 200°C, which was lower than the paleo-temperature (200 to 250°C) of the highest CH$_4$ concentration. The C$_2$H$_6$ to C$_4$H$_{10}$ hydrocarbons were almost absent in residual gas from metapelites.

The concentration of CO$_2$ was highest in the residual gas from shale rocks at paleo-temperatures of less than 200°C (Fig. 4). Some of the CO$_2$ was adsorbed on the surface of mineral grains during pulverization as previously described. The CO$_2$ in residual gas was therefore a part of the total CO$_2$ retained in shale rocks. It decreased drastically from ca. 2000 to 200 μL/gTOC with increasing paleo-temperature. The concentration of CO$_2$ was lower than the concentration of CH$_4$ and H$_2$ in residual gas from metapelites. Hydrogen concentrations were generally very low in shale rocks at paleo-temperatures of less than 200°C. However, the concentration of H$_2$ was higher in the residual gas from metapelites, being in the range of ca. 300 to 1500 μL/gTOC (Fig. 4). These analytical results show that the major component of residual gas from shale rocks and metapelites changes from CO$_2$ to CH$_4$, and then to H$_2$ with the progress of burial diagenesis and metamorphism.
3.3 Isotopic Composition of Residual Gas

The stable carbon and hydrogen isotopic compositions of CH$_4$ and H$_2$ in residual gas in shale and metamorphic rocks were measured to better understand the changes in proportional composition of shale gases as sediment diagenesis and metamorphism progresses. However, the isotopic compositions of residual gas were not determined for some samples with low concentrations of residual CH$_4$ and/or H$_2$. Analytical results of $\delta^{13}$C value of methane ($\delta^{13}$C$_{CH4}$), $\delta^2$H of methane ($\delta^2$H$_{CH4}$), and $\delta^2$H value of H$_2$ ($\delta^2$H$_{H2}$) for shale rocks and metapelites from MITI-Mishima and Kochi district are shown in Tables 1 and 2, respectively. The changes in $\delta^{13}$C$_{CH4}$, $\delta^2$H$_{CH4}$, and $\delta^2$H$_{H2}$ values with increasing paleo-temperature are shown in Fig. 5. The $\delta^{13}$C$_{CH4}$ initially increased from ca. $-45$ to $-30$‰ in the paleo-temperature range of 150 to 230ºC, but then gradually decreased to ca. $-45$‰ in the temperature range of 250 to 600ºC (Fig. 5). The increase and decrease of the $\delta^{13}$C$_{CH4}$ value closely mirrored the increase and decrease of CH$_4$ concentration in residual gas from shale rocks (Fig. 4). The $\delta^2$H$_{CH4}$ was rather scattered, with values ranging from ca. $-205$ to $-150$‰ at paleo-temperatures less than 250ºC. The $\delta^2$H$_{CH4}$ values at paleo-temperatures above 250ºC were in the comparatively narrow range of ca. $-205$ to $-180$‰. The $\delta^2$H$_{H2}$ was in the range of ca. $-850$ to $-650$‰ (Fig. 5), which was significantly lower than the $\delta^2$H$_{CH4}$ values. The $\delta^2$H$_{H2}$ value increased from ca. $-850$ to $-650$‰ and then decreased to ca. $-750$‰ at the paleo-temperature range of 150 to 600ºC. The paleo-temperature of the highest $\delta^2$H$_{H2}$ value was in the range of 300 to 400ºC, which was higher than the temperature of the highest $\delta^{13}$C$_{CH4}$ value.
4. Discussion

4.1 Formation of a Gas-closed System

The highest concentration of CO$_2$ in the early stages of organic maturation (< 200°C) was mainly due to the decarboxylation and other deoxygenations of sedimentary organic matter. The drastic decrease in CO$_2$ concentration with subsequent maturation was considered to be related to the expulsion of pore fluids with dissolved CO$_2$. A large amount of thermogenic CH$_4$ could also be expelled from shale rocks under the open system of CH$_4$ generation. The increase in CH$_4$ concentration in residual gas from the shale rocks of the MITI-Mishima borehole began at a porosity of ca. 5%, which corresponds to a depth of 4500 m and a VR$_o$ of ca. 0.7% (Fig. 2). The mean diameter of pores in marine shale with a porosity of 5% is about 2.5 nm (Okiongbo, 2011; Curtis et al., 2012). Taking into account the effective size of a methane molecule being about 0.40 nm, the mean pore diameter of 2.5 nm would be large enough for CH$_4$ expulsion. Methane entrapment by the shale matrix at a porosity of ca. 5% is linked to low permeability due to the increase in the relative abundance of isolated pores in shale rocks. The concentration of CH$_4$ reached a maximum at VR$_o$ = 2 to 3%, which is the maturity level corresponding to a shale porosity of less than 2% in the MITI-Mishima borehole (JNOC, 1992), suggesting that methane expulsion from shale rock does not occur significantly when the porosity of shale rocks is less than 2%. In Barnett Shale, USA, shale layers with VR$_o$ values > 1.9% have the highest cumulative shale gas production, and production decreases as the VR$_o$ value of shale layers decreases (Rodriguez and Philp, 2010). The maturity level of shale rocks with the highest cumulative shale gas production in Barnett Shale
is approximately consistent with the VR₀ values of shale rocks containing the highest CH₄ concentration in the present study. The highest concentration of CH₄ in residual gas was found at VR₀ = 2 to 3%, suggesting the formation of a closed system for the generation and entrapment of CH₄. This closed system could also trap CO₂ in shale rocks considering the larger molecular size and adsorptivity of CO₂ on the mineral matrix.

Hydrogen, the smallest non-polar molecule, was detected at significant levels in the residual gas. The concentration of H₂ in residual gas began to increase at VR₀ = ca. 1.5% with increasing paleo-temperature. The comparatively large variation in H₂ concentration could be due to the different storage capacity of the rock samples. The higher concentration of H₂ in metapelites suggests the formation of a closed system for the generation and entrapment of H₂. This is consistent with the characteristics of metamorphism, which proceeds under closed-system conditions, with conservation of elements. The H₂ concentration in shale rocks continued to increase in the maturation stage, with a VR₀ = 2 to 4%. The formation of a closed system for H₂ was established in the late stage of metagenesis, which nearly corresponds to the maturation stage of VR₀ = 2 to 3% and shale porosity of c.a. 2% (Figs. 2 and 4).

4.2 Probable Stoichiometry of Gases in Metapelite

Several reactions have been proposed to explain the formation of carbonaceous material such as graphite and diamond under high temperature and pressure in the presence of CH₄, CO₂, and H₂. Among them, the following reactions are the most likely to form graphite from the gas phase during metamorphism
(Galimov et al., 1973; Deines et al., 1980; Hahn-Weinheimer and Hirner, 1981; Deryagin and Fedosayev, 1989; Nabelek et al., 2003; Luque et al., 2012):

\[
\begin{align*}
\text{CH}_4 & \leftrightarrow \text{C (graphite)} + 2\text{H}_2 \quad \text{..... (1)} \\
\text{CH}_4 + \text{CO}_2 & \leftrightarrow 2\text{C (graphite)} + 2\text{H}_2\text{O} \quad \text{..... (2)} \\
\text{CO}_2 + 2\text{H}_2 & \leftrightarrow \text{C (graphite)} + 2\text{H}_2\text{O} \quad \text{..... (3)}
\end{align*}
\]

If carbonate minerals such as calcite and dolomite are abundant, carbonaceous material can be formed as a result of \( \text{CO}_2 \) reacting with \( \text{H}_2 \) and/or \( \text{CH}_4 \) (Reactions (2) and (3)) (Deines et al., 1980; Hahn-Weinheimer and Hirner, 1981). Shale rocks and metapelites in this study contained few carbonate minerals. The concentration of \( \text{CO}_2 \) in residual gas from shale rocks and metapelites in late metagenesis and metamorphism (paleo-temperature > 250ºC) was significantly lower than the concentrations of \( \text{CH}_4 \) and \( \text{H}_2 \) (Fig. 4). Therefore, the formation of graphite resulting from the reaction of \( \text{CO}_2 \) with \( \text{CH}_4 \) (Reaction (2)) or \( \text{H}_2 \) (Reaction (3)) was minor.

The concentration of \( \text{CH}_4 \) tended to decrease during late metagenesis to metamorphism, whereas the concentration of \( \text{H}_2 \) tended to increase (Fig. 4). Taking into account that changes in the composition of residual gas in metapelite proceed under the closed system, the increase in \( \text{H}_2 \) concentrations corresponding to the decrease in \( \text{CH}_4 \) concentrations suggests the conversion of \( \text{CH}_4 \) to graphite and \( \text{H}_2 \) (Reaction (1)). Graphite can be formed from \( \text{CH}_4 \) at elevated temperatures (Galimov et al., 1973; Deryagin and Fedosayev, 1989; Nabelek et al., 2003). Graphite with low crystallinity was detected in shale rocks and low grade metapelites that experienced maximum temperatures of 250 to 400ºC. The atomic H/C ratio of low crystalline
graphite decreased with increasing metamorphic temperature (Fig. 3), suggesting the liberation of CH$_4$ and H$_2$ from poorly ordered graphite as graphitization progressed. The incorporation of CH$_4$ into graphite and the liberation of CH$_4$ from graphite were assumed to occur alongside the progress of graphitization in metapelite.

The overall decrease of CH$_4$ concentration in the temperature range of 250 to 600ºC was ca. 1000 to 1500 µL/gTOC, whereas the overall increase of H$_2$ concentration was ca. 1500 µL/gTOC (Fig. 4). The total amount of H$_2$ that can be generated from CH$_4$ (ca. 1000 to 1500 µL/gTOC) by Reaction (1) is ca. 2000 to 3000 µL/gTOC. Some CH$_4$ or H$_2$ could be consumed by reactions with CO$_2$ (Reactions (2) or (3)). However, this effect is almost negligible because the decrease in CO$_2$ concentration in the temperature range of 250 to 600ºC was quite small compared to changes in the concentration of CH$_4$ and H$_2$. The observed increase in H$_2$ concentration was less than expected. Moreover, H$_2$ can be generated from carbonaceous material during graphitization. The H$_2$ concentration determined in this study was less than that generated in metapelite during metamorphism, suggesting the consumption of H$_2$ by unknown reactions.

Hydrogen could be liberated from H$_2$O at high metamorphic temperatures. Hydroxyl (OH$^-$) is released from hydrous minerals due to successive dehydration during metamorphism. The formation of water due to the dehydration of metamorphic rocks requires hydrogen (H$^+$). Therefore, the dehydration of hydrous minerals such as chlorite and muscovite with increasing metamorphic grade consumes H$_2$. The dehydration of hydrous minerals could be one of the reactions responsible for the significant consumption of H$_2$ during metamorphism.
4.3 Change in Isotopic Composition of CH$_4$ with Graphitization

The enrichment of $^{13}$C in thermogenic CH$_4$ with increasing maturation has been well studied (e.g. Berner and Faber, 1996). The increase in the $\delta^3$C$_{CH_4}$ value from ca. $-45$ to $-30\%$ in the paleo-temperature range from 150 to 230°C ($VR_o = 0.7$ to 2.5%) was assumed to be due to the addition of thermogenic CH$_4$, which is rich in $^{13}$C, with the progressive thermal cracking of bitumen and kerogen. The $\delta^2$H$_{CH_4}$ values at paleo-temperatures in the range of 150 to 250°C were variable. The initial $\delta^2$H values of sedimentary organic matter are related to source organisms, with significant variation in the range of $-400$ to $-100\%$ (e.g., Chikaraishi and Naraoka, 2007; Sachse et al., 2010). The $\delta^2$H values of algae and higher plants are also related to hydrology, humidity, or aridity (e.g. Tipple and Pagani, 2010; Yang et al., 2011). In addition, hydrogen exchange between interstitial water and sedimentary organic matter in the early stage of diagenesis has been suggested (Schimmelmann et al., 2006; Kikuchi et al., 2010). The significant variation of $\delta^2$H$_{CH_4}$ values at paleo-temperatures of less than 250°C could be due to these various factors related to the $\delta^2$H values of sedimentary organic matter. The $\delta^2$H$_{CH_4}$ values of the samples at paleo-temperatures above 250°C were comparatively low, ranging from $-180$ to $-210\%$. The decrease in $\delta^2$H$_{CH_4}$ values at paleo-temperatures above 250°C seems to be associated with a decrease of $\delta^{13}$C$_{CH_4}$ values in the stages of late metagenesis to metamorphism (Fig. 5).

Graphite synthesized from CH$_4$ in the laboratory is enriched in $^{12}$C compared to the initial CH$_4$ (Galimov et al., 1973; Deryagin and Fedosayev, 1989). However, this isotopic fractionation is kinetic and largely depends on the rate of graphite formation. The enrichment of $^{12}$C during graphite formation from CH$_4$ decreases as the growth rate decreases and has not been observed at low growth rates in the laboratory.
(Galimov et al., 1973; Deryagin and Fedosayev, 1989). According to Luque et al. (2012), graphite generated from CO$_2$–rich fluid shows a progressive $^{13}$C enrichment with crystal growth, whereas graphite generated from CH$_4$–rich fluid shows the opposite pattern, being progressively enriched in $^{12}$C. These observations suggest that, at low growth rates under natural conditions, the heavier $^{13}$CH$_4$ is easier to incorporate into the growth region of graphite crystals than the lighter $^{12}$CH$_4$. According to Rayleigh isotopic fractionation, the progressive enrichment of $^{12}$C in graphite with crystal growth is generally accompanied by the $^{12}$C enrichment of CH$_4$ in the closed system. The $\delta^{13}$C$_{\text{bulk}}$ values of some selected shale rocks and metapelites were in the range of ca. –27 to –21‰ (Table 2). The $\delta^{13}$C$_{\text{bulk}}$ value increased systematically with increasing metamorphic grade (Fig. 6), which is consistent with the results of previous studies (Hoefs and Frey, 1976; Morikiyo, 1986). The increase in the $\delta^{13}$C$_{\text{bulk}}$ value was assumed to be due to the liberation of $^{12}$C-rich CH$_4$ from carbonaceous material. However, the concentration of CH$_4$ decreased with increasing metamorphic temperature, suggesting that the decrease of the $\delta^{13}$C$_{\text{CH}_4}$ value in the residual gas in metapelite was due both to the incorporation of $^{13}$C-rich CH$_4$ into carbonaceous material and the liberation of $^{12}$C-rich CH$_4$ from carbonaceous material. The incorporation and liberation of CH$_4$ could be responsible for the decrease in CH$_4$ concentration and the $\delta^{13}$C$_{\text{CH}_4}$ value with increasing metamorphic temperature. The $\delta^{2}$H$_{\text{CH}_4}$ values at higher metamorphic grades were comparatively low, in the range of –185 to –205‰, although the variation in the $\delta^{2}$H$_{\text{CH}_4}$ value with increasing metamorphic grade was not confirmed (Fig. 5).

4.4 Origin of Hydrogen Gas in Metapelite
The $\delta^2$H$_{\text{H}_2}$ value of residual gas was in the range of ca. –850 to –650‰ (Fig. 5). This $\delta^2$H$_{\text{H}_2}$ value was quite low compared to those of sedimentary organic matter, which generally range from –100 to –350‰ (e.g. Schimmelmann et al., 2006, Kikuchi et al., 2010). $^2$H-depleted H$_2$ gas, with $\delta^2$H values of less than –500‰, has been found in H$_2$-rich gases related to the serpentinization of ophiolite (Neal and Stanger, 1983; Sano et al., 1993), deep gases (Jeffrey and Kaplan, 1988), gases from geothermal areas (Mayhew et al., 2013), and fault gases (Sugisaki et al., 1983; Randolph et al., 1985). Hydrogen gas characterized by low $\delta^2$H values (< –500‰) is thought to be generated physically by water-rock interactions to form the silanol functional group and/or chemically by the reduction and dissociation of H$_2$O (Saruwatari et al., 2004; Mayhew et al., 2013). Sedimentary organic matter is another important source of H$_2$ in the shallow crust of the earth. However, there are few reports of the isotopic composition of H$_2$ derived from the dissociation of carbon-hydrogen bonds in sedimentary organic matter. Hydrogen liberated during dehydrogenation and incorporated during hydrogenation is substantially depleted in $^2$H due to the large kinetic isotope effects (ca. 600‰) associated with the enzymatic biochemical reactions (Luo et al., 1991; Chikaraishi et al., 2004). A similar extent of isotopic fractionation of hydrogen during the thermal dissociation of carbon-hydrogen bonds is expected, since the mechanism of enzyme catalysis is similar in principle to other types of chemical catalysis. The dissociation energy of the C-$^2$H bond is significantly larger than that of the C-$^1$H bond, suggesting a large isotopic fractionation during the dissociation of hydrogen from carbon-hydrogen bonds. The significantly low $\delta^2$H$_{\text{H}_2}$ values ranging from –800 to –650‰ (Fig. 5) could be due to the large isotopic fractionation associated with the dissociation of hydrogen from sedimentary organic matter.
Li et al. (2015) have performed the laboratory open-system pyrolysis experiments for liberation of H₂ and CH₄ from organic matter in shales and coals. The results showed that the H₂ liberation proceeds in association with cracking of hetero-bonds, demethylation, aromatization, and condensation. The major stage of the H₂ liberation is generally later than that of CH₄ liberation, since the bond energy of C-H bonds is significantly larger than that of C-C bonds. This is consistent with the observation in the present study that the major residual gas in shales and metapelites changes from CH₄ to H₂ with increasing temperature. The liberation of H₂ due to aromatization and condensation proceeds at 400 to 900°C under the heating rate of 0.5°C/min in the laboratory (Li et al., 2015), while H₂ concentration in the residual gas of shales started to increase at paleo-temperature of ca. 200°C. This difference can be explained by the kinetics of aromatization and condensation under different time-temperature conditions. The compositional change of residual gas during diagenesis and metamorphism suggests the organic origin of H₂ in the residual gas of shales and metapelites.

Hydrogen can also be generated from low-crystalline graphite. However, the H₂ generated by the graphitization of carbonaceous material becomes gradually richer in ²H because the C-¹H bond is easier to break during metamorphism relative to the C-²H bond. The expected change in the δ²H value of H₂ from low-crystalline graphite with graphitization did not seem to be consistent with the observed change in the δ²H₂ value of residual gas. The atomic H/C of low crystalline graphite decreased from 0.2 to 0.05 in the temperature range of 300 to 600°C (Fig. 3). The decrease or no increase in the δ²H value of H₂ in residual gas suggests that the decrease in the atomic H/C of graphite was due not only to the dissociation of C-H bonds, but was primarily
due to the liberation of CH₃ radicals as a result of the breaking of the C-C bond in low-crystalline graphite. The overall decrease or no increase in the δ²H value of H₂ in residual gas in the δ²H₂ value during late metagenesis to metamorphism could be mostly related to the liberation of H₂ from CH₄ with graphitization. The slight change in both the δ²H₂ and δ¹³C CH₄ values with increasing metamorphism suggests that, compared to ¹²C¹H₄, the isotopically heavier ¹³C¹H₄ and ¹²C¹H₃²H are easier to incorporate into graphite crystal planes.

The consumption of H₂ associated with the dehydration of hydrous minerals was likely to compensate for the low concentration of H₂ in residual gas of metapelite. The difference in the dissociation energy between the ¹H-¹H and ¹H-²H bonds was small compared to the difference between the C-¹H and C-²H bonds, suggesting that the H₂ dissociation had a small influence on the δ²H₂ value. On the other hand, H-isotope exchange between H₂ and H₂O is known to occur (Arnason, 1977; Horibe and Craig, 1995). The δ³H values of H₂O in metamorphic hydrous minerals such as biotite, muscovite, and amphibole are comparatively higher at more than −150‰ (Kuroda et al., 1978; Morikiyo, 1986). The δ²H₂ value therefore increases in association with the H-isotope exchange between H₂ and H₂O. However, the δ²H₂ value of residual gas in metapelite is quite low, in the range of −650 to −750‰. According to Horibe and Craig (1995), the very low δ²H₂ value cannot be explained by the isotope exchange between H₂ and H₂O at temperatures above 300°C. These suggest that δ²H₂ value is not directly related to the H₂ abundance and H-isotope exchange between H₂ and H₂O. The concentration of H₂ and its δ²H₂ value are related to the various reactions such as hydrogen dissociation from organic matter and H₂O, graphitization, dehydration of hydrous minerals, and hydrogen exchange among
hydrogen-containing compounds. However, hydrogen isotope exchange and fractionation associated with these reactions during diagenesis and metamorphism are still unclear. More detailed study on the behavior of H$_2$ and the change of $\delta^2$H$_{H2}$ value with graphitization under closed-system condition is required for understanding H$_2$ of organic origin in the deep subsurface.

5. Conclusions

The major component of the residual gas in shales and metapelites changed systematically from CO$_2$ to CH$_4$ and to H$_2$ during diagenesis and metamorphism. H$_2$ is the most abundant gas in metapelite. This order is consistent with the liberation of CH$_4$ and H$_2$ from sedimentary organic matter examined by laboratory experiments. The significantly lower $\delta^2$H$_{H2}$ values, ranging from $-800$ to $-650\%$, can be interpreted as arising from the isotopic fractionation associated with the dissociation of hydrogen from carbon-hydrogen bonds. These observations suggest that a significant amount of H$_2$ gas is derived from sedimentary organic matter. The increase of $\delta^{13}$C$_{CH4}$ value of residual gas with increasing maturation during metagenesis is consistent with the change of $\delta^{13}$C value of thermogenic CH$_4$. The $\delta^{13}$C$_{CH4}$ value of residual gas, however, tended to decrease with graphitization. The incorporation of $^{13}$C-rich CH$_4$ into low-crystalline graphite is thought to be responsible for the decreases in CH$_4$ concentration and $\delta^{13}$C$_{CH4}$ value with increasing metamorphic temperature. The decrease or no increase in the $\delta^2$H$_{H2}$ values during graphitization suggests that the decrease in the atomic H/C of graphite was due not only to the dissociation of C-H
bonds, but was primarily due to the liberation of CH\textsubscript{3} radicals as a result of the breaking of the C-C bond in low-crystalline graphite. However, hydrogen isotope exchange and fractionation during diagenesis and metamorphism are still unclear. More detailed study on the behavior of H\textsubscript{2} and the change of \(\delta^2\text{H}_{\text{H}_2}\) value with maturation and graphitization under closed-system condition will provide clues for understanding H\textsubscript{2} of organic origin in the deep subsurface. On the other hand, the observed H\textsubscript{2} concentration was less than expected from the decrease of atomic H/C of low-crystalline graphite, suggesting the consumption of H\textsubscript{2} by dehydration of hydrous minerals during metamorphism. The present study also provides useful information regarding the gases released from shales and metapelites in association with their destruction and deformation in the mobile belt. Fault gases often contain a significant amount of H\textsubscript{2} depleted in \(^2\text{H}\). A portion of the H\textsubscript{2} in fault gases in the metamorphic belt may be derived from H\textsubscript{2} released from metapelites during their destruction.

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1502-1508.


Table Captions:

**Table 1** Total organic carbon (TOC) concentration, residual gas composition, and isotopic composition of residual gas of shales from MITI-Mishima borehole. The present-day temperature is almost identical to the maximum temperature of heating.

**Table 2** Mean vitrinite reflectance (VR_o), total organic carbon (TOC), carbon and hydrogen concentrations and carbon isotopic compositions of kerogen and graphite, residual gas composition and carbon and hydrogen isotopic compositions of residual gas of shales and metapelites in Kochi district. Maximum heating temperature (Max. Heating Temp.) is estimated based on VR_o and metamorphic minerals.

Figure Captions:

**Figure 1** Locations of MITI-Mishima borehole and sampling sites of shales and metamorphic rocks in Kochi district, Shikoku, Japan. The core and cuttings samples of shales were obtained from the MITI-Mishima borehole in the Niigata Prefecture.

**Figure 2** Changes in TOC concentration, cutting gas composition, porosity, \( \text{CH}_4 \)–\( \text{C}_3\text{H}_8 \) concentrations in residual free gas, vitrinite reflectance, sterane isomer ratio, and bottom hole temperature with depth in the MITI-Mishima
borehole (JNOC, 1992; Suzuki et al., 2013). Residual gas was obtained by pulverization of cuttings and core samples. Hz; Haizume Formation, NY; Nishiyama Formation, SY; Shiiya Formation, U.TD; Upper Teradomari Formation, L.TD; Lower Teradomari Formation, NT; Nanatani Formation.

Figure 3 Changes in the atomic H/C ratio of carbonaceous material (kerogen and graphite) in shales and metapelites with increasing temperature. The samples are from Shimanto, Chichibu, Mikabu greenstone, and Sanbagawa metamorphic belts in Kochi district. VRₒ (%) is vitrinite reflectance.

Figure 4 Concentration changes of (A) CO₂, (B) CH₄ and C₂H₆, and (C) H₂ in the residual gas of shales and metapelites with increasing temperature. The samples are from MITI-Mishima borehole in the Niigata basin, Shimanto, Chichibu, Mikabu greenstone, and Sanbagawa metamorphic belts in Kochi district (Fig. 1). VRₒ (%) is vitrinite reflectance. The major component of residual gas in shales and metapelites changes from CO₂ to CH₄ and then to H₂ with increasing maximum temperature of heating.

Figure 5 Changes in carbon and hydrogen isotopic compositions of (A) CH₄, (B) CH₄ and (C) H₂ in the residual gas from shales and metapelites with increasing temperature. The samples are from MITI-Mishima borehole in the Niigata basin, Shimanto belt, Chichibu belt, Mikabu Greenstone belt, and Sanbagawa metamorphic belt in Kochi district. VRₒ(%) is vitrinite reflectance.
**Figure 6** Change in the $\delta^{13}C$ value of carbonaceous material (kerogen and graphite) in shales and metapelites with increasing temperature. The samples are from Shimanto, Chichibu, Mikabu greenstone, and Sanbagawa metamorphic belts in Kochi district. $VR_o$ (%) is vitrinite reflectance.
Table 1. Total organic carbon (TOC) concentration, residual gas composition, and isotopic composition of residual gas of shales.

<table>
<thead>
<tr>
<th>Depth (m)</th>
<th>Formation</th>
<th>TOC (%)</th>
<th>Present CO₂ (µL/g TOC)</th>
<th>CH₄ (µL/g TOC)</th>
<th>C₂H₆ (µL/g TOC)</th>
<th>H₂ (µL/g TOC)</th>
<th>δ¹³C CH₄ (%)</th>
<th>δ²H CH₄ (%)</th>
<th>δ²H H₂ (%)</th>
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Sy F.; Shiiya Formation, U. Td. F.; Upper Teradomari Formation, L Td. F.; Lower Teradomari Formation, Nt. F.; Nanatani Formation
Table 2. Mean vitrinite reflectance (VRo), total organic carbon (TOC), elemental and carbon isotopic compositions of kerogen and graphite, residual gas composition, and isotopic composition of residual gas of shales and metapelites in Kochi district. Maximum heating temperature (Max. Heating Temp.) is estimated based on VRo and metamorphic minerals.

<table>
<thead>
<tr>
<th>Geologic Belt</th>
<th>Group or Metamorphic Zone</th>
<th>Sample No.</th>
<th>VRo (%)</th>
<th>Max. Heating Temp. (ºC)</th>
<th>TOC (%)</th>
<th>Kerogen and graphite</th>
<th>CO₂ (µL/gTOC)</th>
<th>CH₄ (µL/gTOC)</th>
<th>C₂H₆ (µL/gTOC)</th>
<th>H₂ (µL/gTOC)</th>
<th>δ¹³C CH₄ (‰)</th>
<th>δ²H H₂ (‰)</th>
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Dry ash free; tr: trace; n.d.: not determined
Fig. 1
Fig. 3

[Graph showing the relationship between Atomic H/C and Temperature (°C), with distinct zones marked for Chlorite, Garnet, and Biotite.]

VRo (%)

0.5 1 2 3 4
Fig. 4

(A) $\text{CO}_2$

(B) $\text{CH}_4$, $\text{C}_2\text{H}_6$

(C) $\text{H}_2$

Temperature (°C)

Shale Porosity (%)

VRo (%) 0.5 1 2 3 4

Chlorite Zone

Garnet Zone

Biotite Zone
Fig. 5

(A) $\delta^{13}C_{\text{CH}_4}$

(B) $\delta^{2}H_{\text{CH}_4}$

(C) $\delta^{2}H_{\text{H}_2}$

Temperature (°C)

Chlorite Zone
Garnet Zone
Biotite Zone

VRd(%) 0.5 1 2 3 4

VRc(%) 0.5 1 2 3 4

VRo(%) 0.5 1 2 3 4
Fig. 6