



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 H₂, CH₄, and CO₂ 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 100–600 °C 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 CO₂, CH₄, to H₂ in this order with increasing temperature. Drastic decrease of CO₂ derived from decarboxylation of sedimentary organic matter is due to the expulsion of pore fluids with dissolved CO₂. The CH₄ concentration in residual gas subsequently increases with organic maturation and reaches the maximum at paleo-temperature of ca. 250 °C. The CH₄ concentration decreases during late metagenesis to metamorphism probably due to the formation of H₂ gas and graphite. The H₂ starts to increase at paleo-temperature of ca. 200 °C. The H₂ gas is the most abundant gas in residual gas of metapelite. The δ²H value of H₂ in shales and metapelites is quite low to be in the range of ca. –850 to –650‰. The change of major residual gas from CH₄ to H₂ with increasing paleo-temperature and the significantly low δ²H values of H₂ suggest that H₂ gas in shales and metapelites is largely derived from liberation of hydrogen in organic matter.

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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 (Jeffery 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

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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 100–600 °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 summarized 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

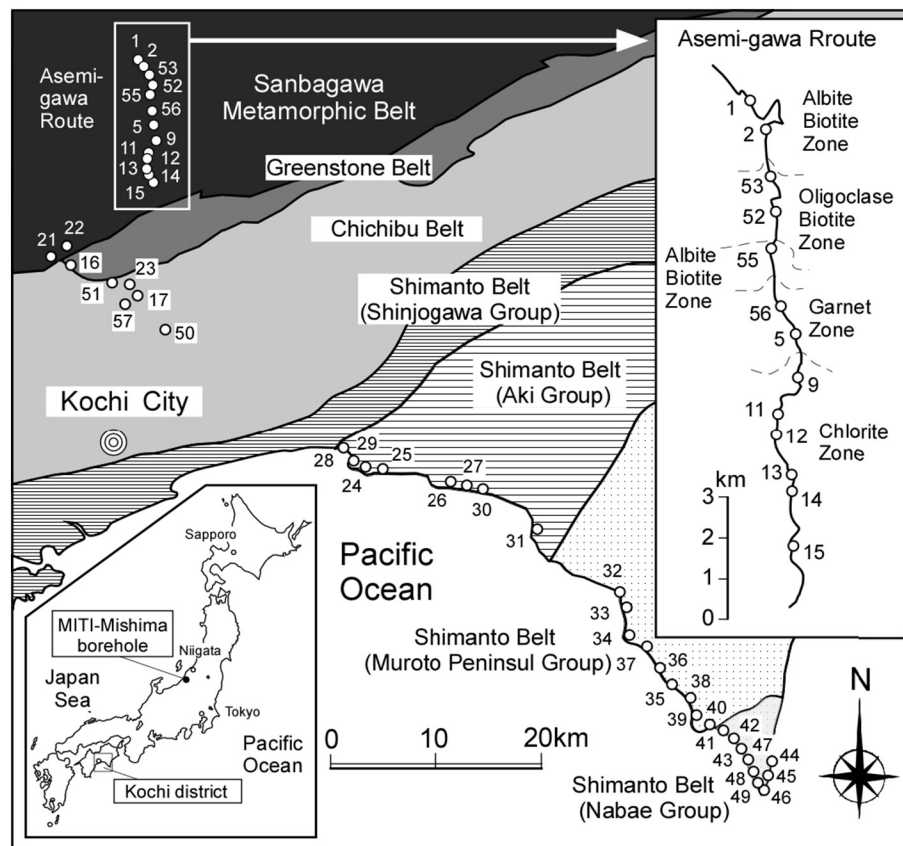


Fig. 1. Locations of MITI-Mishima borehole and sampling sites of shales and metamorphic rocks in Kochi district, Shikoku, Japan. The core and cuttings samples of shales were obtained from the MITI-Mishima borehole in the Niigata Prefecture.

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