

Thematic Article

Behavior of gases in the Nojima Fault Zone revealed from the chemical composition and carbon isotope ratio of gases extracted from DPRI 1800 m drill core

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Abstract An 1800 m borehole was drilled into the Nojima Fault Zone at Ogura, Awaji Island, Hyogo prefecture, Japan. The chemical compositions and isotope ratios of gases extracted from the drill core were investigated. Major components were carbon dioxide (CO₂) and methane (CH₄). Microcracks in granodiorite outside the fracture zone were occupied mainly by CO₂, and this CO₂ is interpreted to have generated biogenically at shallow depths based on the measured $\delta^{13}\text{C}$ value of -17 to -22 . The CO₂ gas was probably transported with underground water to deeper portions to fill microcracks in the basement granodiorite with CO₂. However, the pores in the fracture zone are occupied predominantly by CH₄. The ratio of CH₄ to ethane (C₂H₆), 80 to 100, and $\delta^{13}\text{C}$ of CH₄, -40 to -52 , suggest that CH₄ and C₂H₆ formed by the thermal decomposition of organic materials at temperatures above 75°C. We interpret that they originated at depths from organic materials and migrated upwards through the fault zone. It is interpreted that the concentration of CO₂ in the fracture zone has decreased by the replacement with CH₄ and/or by the consumption of CO₂ in fault clay minerals. Although hydrogen (H₂) and helium (He) were minor components of the gases from cores, they increased in quantity in the fracture zone. High concentration of H₂ in the fracture zones is consistent with the idea that H₂ was generated by radical reactions on the fresh surface of fractured rocks during the earthquake. The ³He/⁴He ratio of 0.723 Ra in the fracture zones suggests that He is of radiogenic origin; that is, it is not from the mantle.

Key words: earthquake fault, earthquake geochemistry, fault drilling, fault gas, Hyogo-ken Nanbu earthquake (Kobe earthquake), Nojima Fault, underground gas.

INTRODUCTION

Hyogo-ken Nanbu earthquake (Kobe earthquake) occurred on January 17, 1995 in the Hanshin–Awaji area of Japan. In the northern part of Awaji Island, surface fault ruptures formed close to or almost parallel to the Nojima active fault (Fig. 1; e.g. Lin *et al.* 1995). Aftershock distribution sug-

gests that the Nojima Fault is the surface trace of the earthquake source fault (Disaster Prevention Research Institute 1995). Several boreholes were drilled into the Nojima Fault Zone in order to study the fault zone at various depths. A 1800 m deep drilling was conducted by Disaster Prevention Research Institute, Kyoto University, at Ogura, approximately 10 km to the south-west of the epicenter near the fault (DPRI 1800 m drilling; Ando 2001). The location of the drilling site is shown in Fig. 1. We used core specimens for investigating the natural gases and their behavior in the fault zone.

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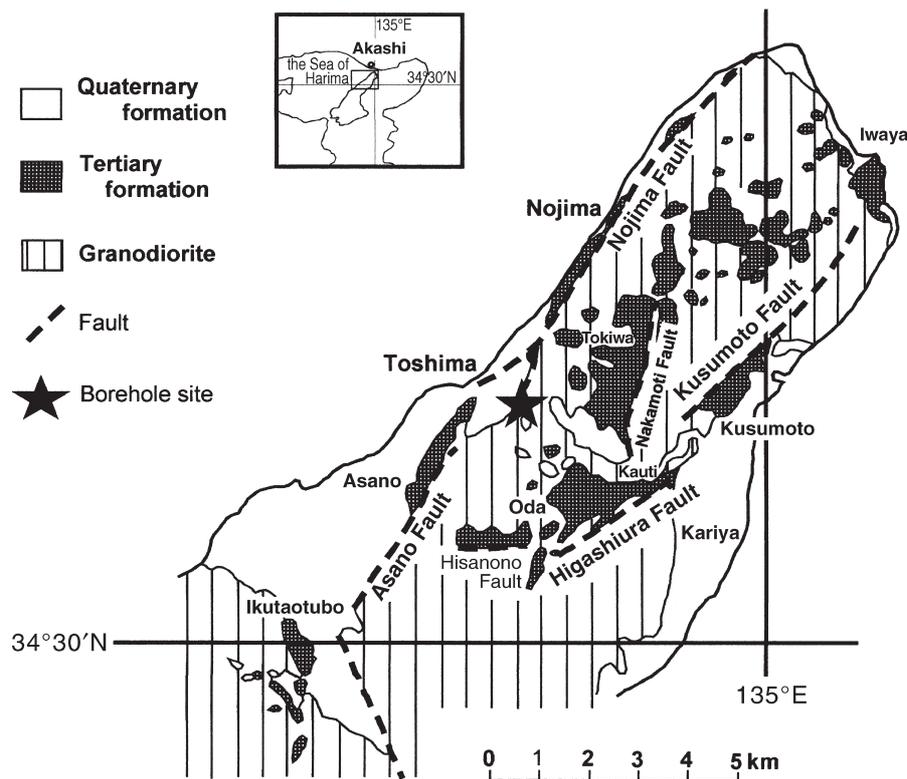


Fig. 1 Location of Disaster Prevention Research Institute, Kyoto University (DPRI) 1800 m drilling site (★) and simplified geological map (adapted from Mizuno *et al.* 1990) of the northern part of Awaji Island. Surface traces of active faults are shown as dashed lines.

The borehole was made approximately 450 m away from the fault on the surface and with an inclination so as to cross the fault zone at a depth of approximately 1800 m. On the basis of observations of core specimens, Kobayashi *et al.* (1999) have suggested that the DPRI 1800 m borehole did not penetrate through the main fault zone completely but reached the marginal fractured zone around it.

Fracture zones formed by fault movement become a path for fluids. Fracture zones also can be a place for the generation and consumption of gases and ions in water. In fact, high concentrations of some ions and dissolved gases have been detected at and around active faults in the past (e.g. Sugisaki *et al.* 1980; Wakita *et al.* 1980; Sato *et al.* 1986). It is also reported that marked changes in concentrations of some chemical species in fluids from underground occurred before the 1995 Hyogo-ken Nanbu earthquake. Concentrations of chloride and sulfate ions in underground water from two wells around the epicentral area increased before the earthquake (Tsunogai & Wakita 1995). At another site located approximately 30 km north-east of the hypocenter, radon concentration in groundwater also increased before the earthquake (Igarashi *et al.* 1995). On

Awaji Island, a geochemical anomaly in underground gas before the earthquake occurred has not been reported.

In the present study, we analyzed the chemical composition of underground gases in core specimens obtained from deep fracture zones associated with the Nojima Fault. We also analyzed the carbon isotope ratios of CH_4 , CO_2 and CaCO_3 , and determined the spatial distribution and behavior of characteristic gases in and around the fracture zone. This is the first time, to our knowledge, that gas from cores obtained from deep fracture zones have been analyzed shortly after an earthquake occurrence.

METHODS

GAS SAMPLING

Approximately 500 gas specimens were taken from drilling cores immediately after retrieving them from the bottom of the borehole at the drilling site. Because the drilling head was stuck at a depth of 1712 m, branch drilling was made nearly parallel to the first drilling hole. Therefore, we obtained two sets of core specimens: 1250–

1710 m from the first borehole (borehole no. 1) and 1400–1736 m from the second borehole (borehole no. 2). We were able to obtain gas specimens successfully from cores of depth intervals 1410–1710 m of borehole no. 1, and 1423–1430 m and 1536–1736 m of borehole no. 2, but we were unable to obtain gas specimens from any other depth intervals. The cores used in the present study were retrieved during June and July 1996 for borehole no. 1, and September and October 1996 for borehole no. 2, approximately 1.5 years after the earthquake.

A piece of core specimen measuring 0.1–0.2 m in length was used for each gas sample extraction. One piece of core was selected from every 1 m depth interval. Air cannot enter the core because the pressure of the gas in the core is greater than atmospheric pressure. However, gathering gas samples is very difficult at the drill site because the gas volume; that is, the total volume of cracks, in a core is very small. Therefore, we carried out the following procedure. First, within several minutes of retrieving the core from the borehole, the core surface was washed with distilled water and packed in a soft plastic bag with approximately 20 mL of air. The bag was placed in a desiccator, which was evacuated by a vacuum pump (Fig. 2). This causes the gas in the core specimen to expand and move out of the specimen and mix with the 20 mL of air in the bag. Next, a valve was opened to let in air into the desiccator (but not in the bag), resulting in the pressure of the gas in the bag reaching equilibrium with the atmospheric pressure. Approximately 20 mL of mixed gas was left in the plastic bag. These procedures for evacuation and release were repeated three times. Mixed gas for analysis was removed from the plastic bag using a syringe.

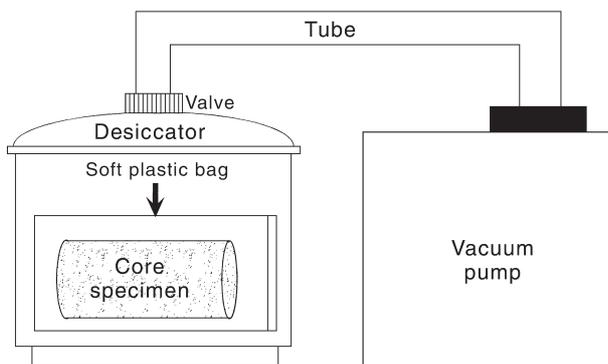


Fig. 2 Schematic drawing of a device for extracting gas from core specimens.

MEASUREMENTS

Chemical compositions of gas samples were analyzed using gas chromatography. Concentrations of CH_4 , CO_2 , H_2 , C_2H_6 , and He were analyzed from borehole no. 1 specimens, and concentrations of CH_4 , CO_2 , C_2H_6 , and CO from borehole no. 2 specimens.

Carbon isotope ratios ($\delta^{13}\text{C}$) of CO_2 , CH_4 and C_2H_6 were analyzed using the irmGC/C/MS system at the Laboratory for Earthquake Chemistry, University of Tokyo (Tsunogai *et al.* 1998). The helium isotope ratio ($^3\text{He}/^4\text{He}$) was measured using a mass spectrometer (VG 5400; VG Isotopes, Manchester, UK) at the same laboratory. Isotope ratios ($\delta^{13}\text{C}$) of calcite (CaCO_3) from calcite veins in core specimens were measured using a mass spectrometer (MAT250; Bremen, Germany) at the Department of Geology, Shinshu University. Measurement errors of the gas chromatographs estimated from repeatability was ± 0.5 ppm for He, H_2 and CO_2 , ± 2 ppm for C_2H_6 , and ± 5 ppm for CH_4 . Errors for mass spectrometers are less than $\pm 0.1\%$.

Variation in concentrations as a result of the variable mixing ratio of air cannot be disregarded, and the absolute values of concentrations cannot be used for discussion. Thus, the ratios between gas concentrations will be used, which will be described in the next section. In the case of isotope measurements, CO_2 samples with concentrations of more than 3000 p.p.m. were used for analysis. CO_2 mixed from air does not give a practical significant effect because CO_2 concentration in air is 360 p.p.m. As a result, the accuracy of the measured carbon isotope ratio is less than $\pm 1\%$. In contrast, the concentration of He in specimens was not as large as for CO_2 . As the isotope ratio of He is more affected by air mixing than that of CO_2 , the isotope ratio of He can only be used for qualitative discussions.

RESULTS

CLASSIFICATION OF CORE SPECIMENS

Core specimens are granodiorite composed of quartz, orthoclase, plagioclase, biotite, and small amounts of amphibole (Matsuda *et al.* 2001). Specimens were classified visually into four groups based mainly on the degree of *in situ* fragmentation and alteration; (i) fresh core specimens with no fragmentation and alteration; (ii) few fracture surfaces are observed and clouded feldspar appears, but

granitic texture still remains; (iii) many fracture surfaces are observed and a part of the core specimen is brecciated. Feldspars appear clouded; and (iv) fault breccias or clay with gray-white color.

The degree of fragmentation of core specimens was assigned a value of 1–4 for each specimen according to this classification. Figure 3a shows the variation in the degree of core fragmentation with depth. The depth value in the figure is the length measured along the borehole from the surface. The length value is actually larger than the real depth by approximately 5% because of the borehole's inclination. Figure 3a shows that the degree of fragmentation is high at depths shall-

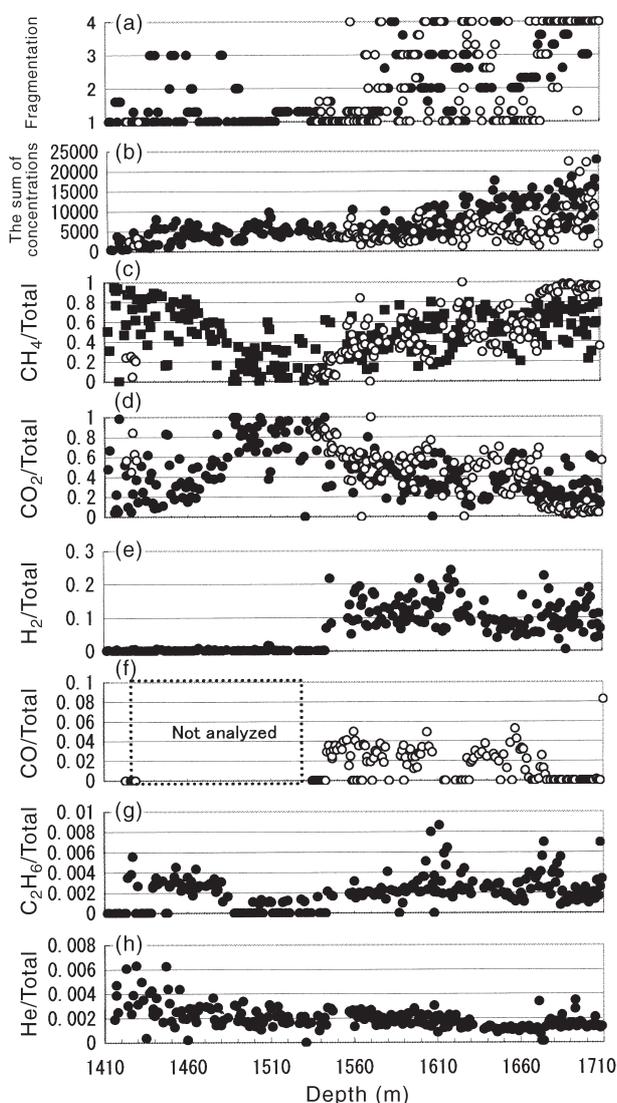


Fig. 3 Variation in the concentrations of extracted gases with depth. (a) Degree of fragmentation of core specimens from weak (1) to strong (4) fragmentation. (b) Total amount of gas concentration of ($\text{CH}_4 + \text{CO}_2 + \text{H}_2 + \text{C}_2\text{H}_6 + \text{He}$) in ppm. (c–g) Concentration of each measured gas relative to the total gas concentration.

lower than 1480 m and deeper than 1560 m. In the present report, the interval between 1410 m and 1480 m will be referred to as the 'subfracture zone', and the interval deeper than 1560 m will be referred to as the 'fracture zone'.

CHEMICAL AND ISOTOPE ANALYSES OF GASES

As mentioned earlier, each gas sample is a mixture of a very small amount of intrinsic underground gas and 20 mL of air. Therefore, the major components of air, such as nitrogen (N_2), oxygen (O_2), and argon (Ar) occupy the majority of the mixed gas specimens. The concentrations of these gas components are affected very little by the underground gas and, hence, these components can be excluded from the present discussions. Alternatively, concentrations of the gases CH_4 , CO_2 , H_2 , C_2H_6 , CO, and He are much smaller in air than in the intrinsic gas; the concentrations in air are less than 2 p.p.m. for CH_4 , H_2 , C_2H_6 and CO, 5.2 p.p.m. for He, and approximately 360 p.p.m. for CO_2 . Thus, the effect of the gases mixing with the same gases present in air can be ignored in the present discussions.

As it is possible that drilling mud might affect the chemical composition of gas, we gathered drilling mud water into a plastic bag when core specimens were retrieved and analyzed the chemical compositions of its dissolved gases. It was confirmed that the gases from the mud water had almost the same composition as those in air. This is reasonable because surface water is used in drilling mud.

Figure 3b indicates the sum of CH_4 , CO_2 , H_2 , C_2H_6 , CO, and He concentrations. Figure 3b somewhat resembles Fig. 3a in its variation patterns. The sum of these gas concentrations, which are minor in the air, should reflect the volume of pores or cracks in the core specimens; that is, the degree of fragmentation, because the total concentration of gas components reflects the volume of gas extracted from the core specimen. Therefore, we will use the concentration ratio of the gas components relative to the sum of the concentration because the absolute volume of extracted gas is not known.

Figure 3c,g show the concentrations of CH_4 and C_2H_6 , respectively, relative to the sum of CH_4 , CO_2 , H_2 , C_2H_6 , CO, and He concentrations. CH_4 is one of the major components of the extracted gas. Figure 3a,c indicate that CH_4 is rich in the subfracture and fracture zones. The relative concentration of C_2H_6 was far less than that of CH_4 . There

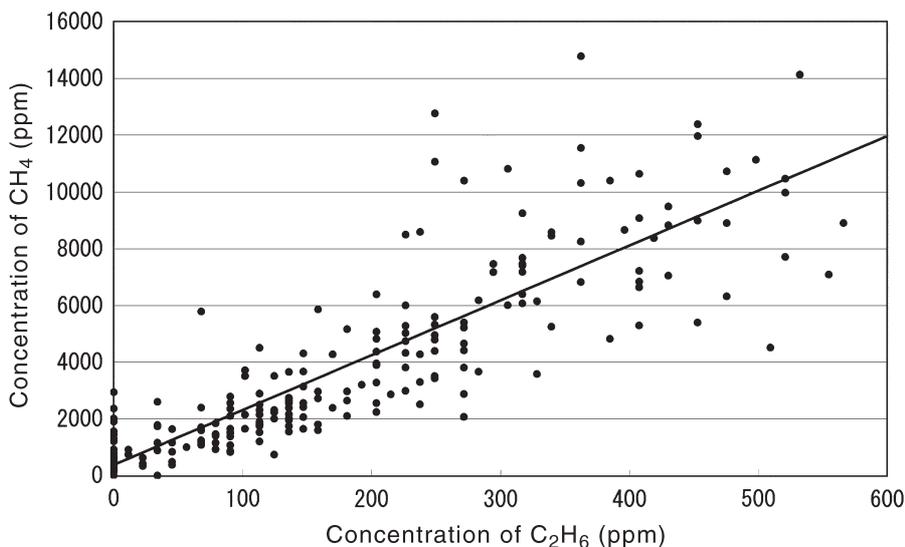


Fig. 4 Relationship between the concentrations of CH₄ and C₂H₆.

Table 1 Carbon and helium isotope ratios

Depth (m)	$\delta^{13}\text{C}[\text{CH}_4]$ (‰)	$\delta^{13}\text{C}[\text{CO}_2]$ (‰)	$\delta^{13}\text{C}[\text{C}_2\text{H}_6]$ (‰)	$\delta^{13}\text{C}[\text{CaCO}_3]$ (‰)	$^3\text{He}/^4\text{He}$	Temperature (°C)
1458				-9.6		45.9
1480	-51	-17				46
1493				-8.8		46.5
1506				-7.2		46.6
1549				-11.9		46.7
1561	-56	-17	-57	-9.7		47.5
1579				-7.9		47.7
1597				-7.4		48
1601				-7.1		48
1630				-7.6		48.3
1642	-52	-17				48.4
1654				-6.9		48.6
1668				-9.3		48.7
1670					0.723 Ra	48.7
1673	-51	-22	-45			48.7
1684	-44	-21	-41			48.7
1689	-48	-19	-42	-8.5		48.7
1694				-8.8		49
1698	-47	-19	-42			49.4
1702				-10.4		
1703	-43	-19	-38			
1709	-42	-20	-37			

is a positive linear relationship between the concentrations of CH₄ and C₂H₆ (Fig. 4).

CO₂ is another major component of the extracted gas, as shown in Fig. 3d, and its concentration is high in non-fragmented rocks. The presence of H₂ in the core obtained from a depth shallower than 1540 m was not detectable and relatively large contents of H₂ were observed at depths greater than 1540 m. Variation in the concentrations of He and CO relative to the sum of CH₄, CO₂, H₂, C₂H₆, CO, and He with depth was small (Fig. 3f,h).

The measured isotope ratios of $\delta^{13}\text{C}[\text{CH}_4]$, $\delta^{13}\text{C}$

[CO₂], $\delta^{13}\text{C}[\text{C}_2\text{H}_6]$, $\delta^{13}\text{C}[\text{CaCO}_3]$, and $^3\text{He}/^4\text{He}$ are listed in Table 1. Nine specimens were measured for $\delta^{13}\text{C}$ of CH₄, CO₂, and C₂H₆, 14 specimens were measured for $\delta^{13}\text{C}$ of CaCO₃, and one specimen for $^3\text{He}/^4\text{He}$.

DISCUSSION AND CONCLUSION

THE ORIGIN OF CH₄ AND C₂H₆

Natural CH₄ gas is produced mainly by one of the following three processes: (i) decomposition of

organic material by bacteria in a reduced environment; (ii) thermal decomposition of organic material at high temperatures ($>75^{\circ}\text{C}$); and (iii) inorganic reaction at high temperatures ($>500^{\circ}\text{C}$) (e.g. Tsunogai 1997). CH_4 originating from each process is characterized by $\delta^{13}\text{C} [\text{CH}_4]$ and a concentration ratio of $\text{CH}_4/\text{C}_2\text{H}_6$ (Bernard *et al.* 1977). The present study's data of isotope and concentration ratios are plotted for $\delta^{13}\text{C}$ against $\text{CH}_4/\text{C}_2\text{H}_6$ (Fig. 5). Areas characterizing thermogenic (thermal decomposition of organic materials) and biogenic (decomposition by bacteria) origins are marked on this graph (from Bernard *et al.* 1977). Figure 5 shows that the data are located in or close to the area of thermogenic origin, suggesting that CH_4 has originated by the thermal decomposition of buried organic materials. The decomposition needs a rather high temperature condition, more than 75°C . Some of the data is plotted outside the area of thermogenic origin, suggesting a small amount of mixing of methane produced by bacteria.

Furthermore, when CH_4 and C_2H_6 are synthesized inorganically, the value of $\delta^{13}\text{C} [\text{CH}_4]$ should be larger than that of $\delta^{13}\text{C} [\text{C}_2\text{H}_6]$ (Sakata 1994). The measured values of $\delta^{13}\text{C} [\text{CH}_4]$ are smaller than those of $\delta^{13}\text{C} [\text{C}_2\text{H}_6]$ (see Table 1). This also supports the interpretation that CH_4 and C_2H_6 are not of inorganic origin.

Because CH_4 is estimated to be a gas produced from organic materials, organic materials must exist near the fracture zone. However, the basement rock is not sedimentary but granitic.

The most likely alternative sources of CH_4 are: (i) recent marine sediments near the Nojima Fault; (ii) an old sedimentary basement, such as the Tanba Group, away from the borehole; and (ii) a

large xenolith of sedimentary rocks in the granodiorite body. In either case, the CH_4 must have generated at depths hotter than 75°C and must have migrated upwards through the fracture zones. Possibly, fracture zones were permeable just after the seismic slip near the fracture zones and CH_4 probably migrated during and after the earthquake.

THE ORIGIN OF CO_2 AND ITS EQUILIBRIUM RELATION TO CaCO_3

The measured values, 22–39, of the isotopic fractionation of ^{13}C between CO_2 and CH_4 are different from the equilibrium value, 55, which was calculated by using Bottinga's equation (Bottinga 1969) under the condition of 50°C , which is the temperature at the bottom of the borehole. Therefore, isotopic fractionation has not reached equilibrium at the bottom of the borehole. The origins of CH_4 and CO_2 should therefore be different.

The measured value of $\delta^{13}\text{C} [\text{CO}_2]$ ranged from -17 to -22 (see Table 1). These values are in the range of CO_2 from organic materials in sediments (Hoefs 1980) and from the present biogenic activity (Tyson 1995), but are different from those of CO_2 at volcanic and geothermal areas (-4 to -9 ; Sano & Marty 1995). Thus, it can be concluded that the origin of the CO_2 in the core specimens is organic material or present biogenic products.

The concentration of CO_2 is high in non-altered and little-fractured rocks, and is low in the fracture zone, indicating that CO_2 exists in the rocks (granodiorite) across wide areas except in the fracture zones. This suggests that the CO_2 comes from the surface because there is no path in the little-fractured rocks for fluids to travel from deeper

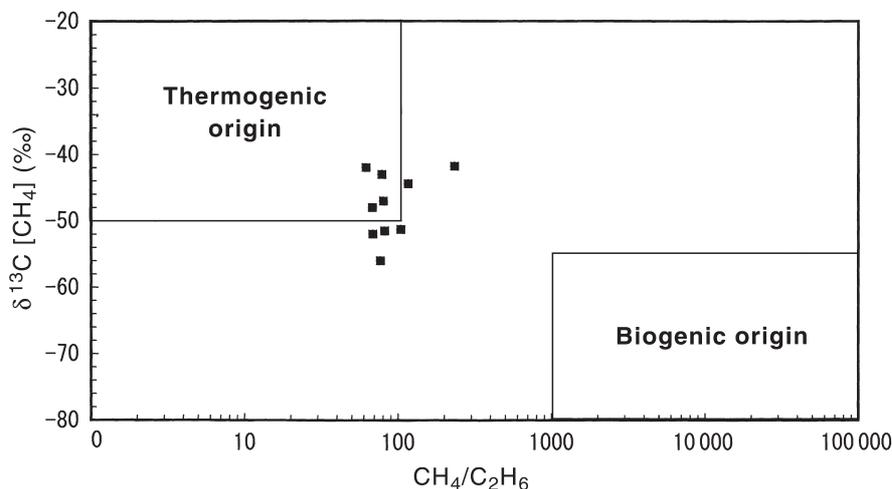
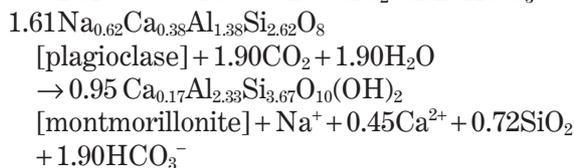
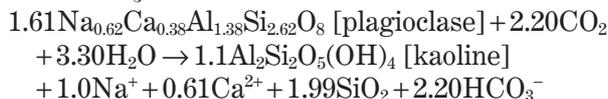
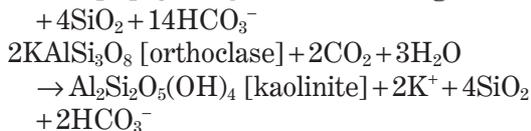
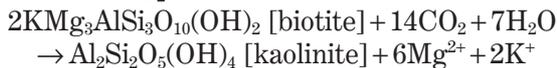


Fig. 5 Relationship between the carbon isotope ratio $\delta^{13}\text{C}$ of CH_4 and $\text{CH}_4/\text{C}_2\text{H}_6$. The thermogenic (thermal decomposition of organic materials) and biogenic (bacterial decomposition of organic materials) regions are also shown (adapted from Bernard *et al.* 1977).

parts. We now address the problem of why CO₂ concentration is low in the fracture zones. As mentioned earlier, CH₄, a dominant gas component in the fracture zones, came from some other place. CH₄ must have migrated through the fracture zones pushing out the pre-existing CO₂ gas. This is probably the major reason for the small concentration of CO₂ in the fracture zones.

Chemical reactions such as those listed below (e.g. Garrels & Christ 1965) will also decrease levels of CO₂ in the fracture zones.



The reactions in the fracture zones proceed more rapidly than those in non-fractured rocks because the total surface area of minerals in the fracture zones is larger than that in fresh rocks. However, alteration of minerals in the DPRI 1800 m cores did not progress very much (e.g. Kobayashi *et al.* 1999). Thus, the contribution of alteration is probably relatively small.

The values of $\delta^{13}\text{C}$ of calcite veins in the core specimens ranged from -6.9‰ to -11.9‰ . We estimated the equilibrium temperature to be approximately 50°C using the data of $\delta^{13}\text{C}$ for CO₂ and CaCO₃ based on the method proposed by Bottinga (1968). This temperature corresponds to the measured value at the approximate depth of 1700 m in the borehole. The estimated depth is almost the same as the depth for the retrieved core specimens, suggesting that CO₂ is in equilibrium with CaCO₃ through pore water in the rocks; hence, we deduce that the groundwater containing CO₂ from the surface has separated the CaCO₃ throughout the rocks (granodiorite).

HIGH CONCENTRATION OF H₂ NEAR FRACTURE ZONES

A high concentration region of H₂ roughly corresponds to the deeper fracture zones (Fig. 3e). This phenomenon is consistent with the model that H₂ is generated by a radical reaction between H₂O

and Si⁻O or Si⁻ radicals that appear on the new surfaces of fractured rocks (Kita *et al.* 1982). A high concentration of H₂ was also detected from the non-fractured zone ranging 1540–1570 m. Any H₂ that has diffused from the fractured zone should be detectable because H₂ has a large diffusion coefficient.

ORIGIN OF He

Helium has two stable isotopes of mass numbers 3 and 4. A large portion of ³He is primordial He, which was trapped in the solid earth at the time of accretion (Clarke *et al.* 1969). ⁴He and a small portion of ³He are produced by nuclear reactions in the solid earth (Morrison & Pine 1955). On the basis of the observed ³He/⁴He ratio, He in natural gases is generally composed of three components: atmospheric He, crustal or radiogenic He, and primordial He derived from the upper mantle. The ³He/⁴He value of magmatic He is higher than that of atmospheric He, whereas the ³He/⁴He value of radiogenic He is smaller than that of atmospheric He (e.g. Sano & Wakita 1985). The measured value of ³He/⁴He from core specimens taken at the depth of 1670.5 m in the fracture zone was 0.723 Ra, which is smaller than that of air (1 Ra). Therefore, the He from the core specimens is not magmatic He but radiogenic He from the granitic basement rocks. This strongly suggests that the fracture zones around the Nojima Fault have not provided upward pathways for gases to travel from the mantle or from magma.

GAS BEHAVIOR IN THE FRACTURE ZONES

Behavior of gases in and around the fracture zones of the fault is summarized in Fig. 6. CO₂ is the major component in the non-fractured zone, indicating that before the 1995 Hyogoken-Nanbu earthquake occurred, microcracks in the granodiorite basement were filled with CO₂, which has been determined as biogenic from its $\delta^{13}\text{C}$ values. In view of their $\delta^{13}\text{C}$ values, CO₂ is in equilibrium with CaCO₃ in the fracture zone. CH₄ and H₂ are the major components of gases in the fracture zones. The ratio CH₄/C₂H₆ and $\delta^{13}\text{C}$ values indicate that CH₄ formed with C₂H₆ by the thermal decomposition of organic materials at depths at temperatures above 75°C. CH₄ seems to have upwelled through the fracture zone after the earthquake. CO₂ in the fracture zone seems to have been pushed out by CH₄. H₂ is generated by radical

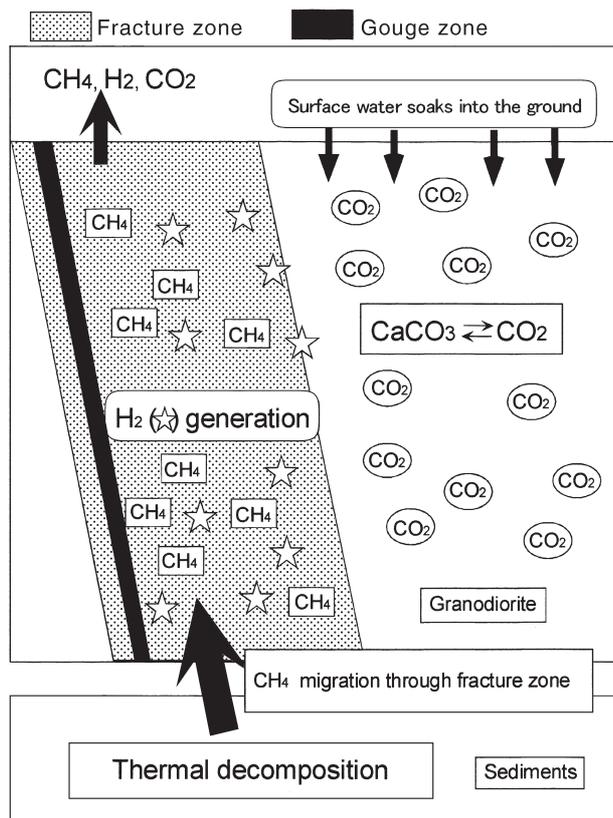


Fig. 6 Proposed model for the underground gas behavior in and around the Nojima Fault. Surface water containing biogenic CO₂ has soaked into the ground and microcracks in the granodiorite body. CH₄, C₂H₆, and H₂ have migrated upwards through the fault zones and replaced CO₂. CH₄ is the dominant gas, which originated by the decomposition of organic material at depths where temperatures are above 75°C.

reactions on the fresh surface of fractured rocks created during the earthquake.

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