





# Effect of Pressure on Hydrogen Isotope Fractionation in Methane during Methane Hydrate Formation at Temperatures Below the Freezing Point of Water

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**Abstract:** Isotopic fractionation of methane between gas and solid hydrate phases provides data regarding hydrate-forming environments, but the effect of pressure on isotopic fractionation is not well understood. In this study, methane hydrates were synthesized in a pressure cell, and the hydrogen isotope compositions of the residual and hydrate-bound gases were determined. The  $\delta^2$ H of hydrate-bound methane formed below the freezing point of water was 5.7–10.3‰ lower than that of residual methane, indicating that methane hydrate generally encapsulates lighter molecules (CH<sub>4</sub>) instead of CH<sub>3</sub><sup>2</sup>H. The fractionation factors  $\alpha_{H-V}$  of the gas and hydrate phases were in the range 0.9881–0.9932 at a temperature and pressure of 223.3–268.2 K and 1.7–19.5 MPa, respectively. Furthermore,  $\alpha_{H-V}$  increased with increasing formation pressure, suggesting that the difference in the hydrogen isotopes of the hydrate-bound methane and surrounding methane yields data regarding the formation pressure. Although the differences in the hydrogen isotopes observed in this study are insignificant, precise analyses of the isotopes of natural hydrates in the same area enable the determination of the pressure during hydrate formation.

Keywords: methane hydrate; hydrogen isotope; isotopic fractionation

# 1. Introduction

Gas hydrates are host–guest compounds comprising hydrogen-bonded water cages containing guest molecules [1]. Natural gas hydrates occur in marine/lacustrine sediments and attract attention as unconventional energy resources [2,3] and greenhouse gas reservoirs [4].

Methane, which is a hydrocarbon, is a major component of natural gas, and the stable isotope ratio of methane is used to estimate its origin [5–8]. Since the stable isotope fractionation of methane caused by phase changes during methane hydrate formation may affect the interpretation of the gas origin, researchers quantitatively evaluate the carbon and hydrogen isotope fractionations of methane using synthetic methane hydrate formation. The hydrogen isotope ratio of the hydrate-bound gas is several ‰ lower than that of the residual gas [9], whereas stable isotope fractionation is negligible in terms of carbon isotope ratios [9,10]. Such stable isotope fractionation of guest gases during gas hydrate formation has been similarly investigated for ethane [9], carbon dioxide [11,12], hydrogen sulfide [13], and nitrogen [14].

In mixed-gas systems such as methane–ethane [15] or methane–carbon dioxide systems [16], ethane and carbon dioxide are more enriched than methane, because the equilibrium pressures of ethane and carbon dioxide hydrates are lower than those of



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**Copyright:** © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). methane hydrates. Even gas hydrates formed using high-purity gases are mixed gas hydrates comprising isotopologues of guest molecules. Similarly, the stable isotope fractionation of guest molecules during the formation of gas hydrates may be explained by the differences in the inclusion properties of isotopologues:  $CH_3^2H$  is less included than  $CH_4$ , with a difference of  $4.8 \pm 0.4\%$  in their  $\delta^2H$  values at 274.2 K [9] ( $\delta$  values are defined in the Section 3), which is consistent with the slightly higher equilibrium pressures of  $CH_3^2H$  hydrates than those of  $CH_4$  hydrates [17]. Additionally, the negligible carbon isotope fractionation of methane during the formation of methane hydrates is consistent with the almost equal equilibrium pressures of the  $^{13}CH_4$  and  $^{12}CH_4$  hydrates [18].

Determination of the effects of temperature and pressure on the stable isotope fractionation of guest gases during gas hydrate formation is useful in reconstructing the environment wherein the natural gas hydrates were formed, e.g., the difference in the stable isotope ratios of hydrate-bound methane and those in the environment yields data regarding the formation depths of natural gas hydrates in submarine/lacustrine sediments and beneath permafrost layers. These data also provide a basis for examining the origins and formation processes of gas hydrates that may occur not only on Earth, but also in other planetary and satellite systems [19–23]. However, the effects of temperature and pressure on the stable isotope fractionation of guest gases during gas hydrate formation have not yet been investigated in detail. In a previous study [9], below the freezing point of water (243.7–265.2 K), the difference in the  $\delta^2$ H values of the residual and hydrate-bound gases was 8–11‰, which exceeds the value (4.8 ± 0.4‰) at 274.2 K. The effect of pressure on stable isotope fractionation is not reported.

The objective of this study is to clarify the effects of temperature and pressure on the stable isotope fractionation factor of hydrogen in methane during the formation of methane hydrate. In this study, we formed synthetic methane hydrate and investigated the differences in the hydrogen isotope ratios of methane in the hydrate-bound gas and residual gas around the crystals over the wide temperature range 223.3–268.2 K. Additionally, we investigated the effects of pressure on the hydrogen isotope fractionation of methane at different formation pressures in the range 1.7–19.5 MPa.

# 2. Results and Discussion

The stable isotope compositions are shown in Figure 1 and Table 1. Methane hydrates are formed in the respective temperature and pressure ranges of 223.3–268.2 K and 1.7–19.5 MPa. The hydrogen isotope ratios of the original (initial), residual, and hydrate-bound gases are  $-154.4 \pm 0.3\%$ ,  $-154.2 \pm 0.5\%$ , and  $-163.4 \pm 1.0\%$ , respectively, suggesting that the hydrate encapsulates lighter methane (Figure 1). As 91.2–99.8% of the methane introduced into the pressure cell remains in the cell as residual gas, the hydrogen isotope ratios of the original and residual gases are similar. The fractionation factor  $\alpha_{\text{H-V}}$ , which is defined in the Section 3 and calculated using these isotope ratio data, is 0.9907  $\pm$  0.0014, which is similar to 0.9893  $\pm$  0.0008 at 243.7–265.2 K and 3.3–5.6 MPa [9]. A total of 2 of the 25 samples were formed over respective formation times of 1 and 3 h (Table 1). Although these formation times are relatively shorter than those of the other samples (formation times of approximately 2 d) and the amounts of hydrates formed are small,  $\alpha_{\text{H-V}}$  remains the same at the same temperature and pressure.

 $\alpha_{\text{H-V}}$  was plotted as a function of the formation temperature, as shown in Figure 2. Over the pressure range of 4–6 MPa,  $\alpha_{\text{H-V}}$  is 0.9900  $\pm$  0.0008 and increases slightly with temperature. Furthermore,  $\alpha_{\text{H-V}}$  varies with the formation pressure, and the pressure dependence of  $\alpha_{\text{H-V}}$  is shown in Figure 3.  $\alpha_{\text{H-V}}$  increases with increasing formation pressure.  $\alpha_{\text{H-V}}$  values at 5 and 20 MPa are approximately 0.990 and 0.993. These results suggest that hydrogen isotope fractionation decreases with increasing formation pressure.



**Figure 1.**  $\delta^2$ H values of the original (initial), residual, and hydrate-bound methane represented using gray squares, blue circles, and green diamonds, respectively.

**Table 1.** Stable isotope compositions of the original (initial), residual, and hydrate-bound gases; the fractions of the residual gases *f*; and the hydrogen isotope fractionation factors  $\alpha_{H-V}$  at various formation temperatures and pressures.

T/K <sup>a</sup>	<i>p</i> /MPa <sup>a</sup>	Original Gas [‰]	Residual Gas [‰]	Hydrate-Bound Gas [‰]	f	$\alpha_{ ext{H-V}}$
224.2	1.7	$-154.1\pm0.5$	$-153.0\pm0.2$	$-162.7\pm0.5$	0.912	$0.9891 \pm 0.0006$
224.8	4.7	$-153.6\pm0.9$	$-153.1\pm0.5$	$-163.4\pm0.7$	0.966	$0.9881 \pm 0.0005$
229.0	8.4	$-154.1\pm0.2$	$-153.9\pm0.2$	$-161.8\pm0.3$	0.981	$0.9907 \pm 0.0005$
228.7	11.7	$-154.0\pm0.2$	$-153.9\pm0.2$	$-160.3\pm0.3$	0.986	$0.9925 \pm 0.0005$
223.3	19.2	$-153.5\pm0.4$	$-153.4\pm0.4$	$-159.4\pm0.4$	0.991	$0.9929 \pm 0.0005$
243.2	1.7	$-154.4\pm0.4$	$-153.3\pm0.3$	$-162.7\pm0.4$	0.941	$0.9892 \pm 0.0004$
243.2	3.2	$-153.8\pm0.2$	$-153.0\pm0.4$	$-162.7\pm0.3$	0.955	$0.9889 \pm 0.0003$
243.2	5.0	$-153.7\pm0.4$	$-153.5\pm0.3$	$-162.3\pm0.3$	0.963	$0.9898 \pm 0.0001$
243.3	5.1	$-153.9\pm0.5$	$-153.4\pm0.4$	$-161.8\pm0.4$	0.967	$0.9902 \pm 0.0007$
243.2	8.8	$-153.7\pm0.2$	$-153.7\pm0.3$	$-161.3\pm0.3$	0.988	$0.9911 \pm 0.0003$
243.2	14.4	$-154.1\pm0.2$	$-153.9\pm0.4$	$-160.4\pm0.5$	0.992	$0.9923 \pm 0.0003$
243.2	16.2	$-154.0\pm0.2$	$-154.0\pm0.3$	$-160.3\pm0.4$	0.990	$0.9926 \pm 0.0002$
243.2	19.5	$-154.2\pm0.3$	$-154.2\pm0.4$	$-160.0\pm0.2$	0.990	$0.9932 \pm 0.0003$
248.1	5.1	$-153.9\pm0.7$	$-153.4\pm0.5$	$-162.2\pm0.6$	0.966	$0.9897 \pm 0.0006$
253.1	4.9	$-154.2\pm0.4$	$-153.6\pm0.1$	$-162.2\pm0.5$	0.962	$0.9901 \pm 0.0006$
258.2	5.0	$-154.1\pm0.5$	$-154.0\pm0.3$	$-162.3\pm0.4$	0.968	$0.9903 \pm 0.0006$
263.1	1.9	$-153.8\pm0.6$	$-153.1\pm0.2$	$-162.0\pm0.6$	0.942	$0.9899 \pm 0.0005$
263.1	2.6	$-154.4\pm0.2$	$-153.3\pm0.3$	$-162.2\pm0.4$	0.944	$0.9898 \pm 0.0003$
263.1	3.2	$-153.7\pm0.6$	$-152.4\pm0.4$	$-161.2\pm0.2$	0.925	$0.9899 \pm 0.0003$
263.1	5.1	$-152.9\pm0.8$	$-152.2\pm1.0$	$-160.7\pm0.9$	0.962	$0.9902 \pm 0.0007$
263.0	5.3	$-154.2\pm0.6$	$-153.8\pm0.6$	$-162.0\pm0.5$	0.998 <sup>b</sup>	$0.9903 \pm 0.0006$
263.0	5.4	$-153.4\pm0.9$	$-153.0\pm1.4$	$-161.0\pm1.2$	0.989 <sup>c</sup>	$0.9905 \pm 0.0007$
262.9	9.1	$-154.2\pm0.3$	$-154.1\pm0.6$	$-161.5\pm0.2$	0.982	$0.9913 \pm 0.0006$
263.1	13.6	$-154.0\pm0.3$	$-153.9\pm0.3$	$-160.0\pm0.5$	0.988	$0.9928 \pm 0.0008$
268.2	5.9	$-153.8\pm0.8$	$-153.8\pm0.9$	$-161.6\pm0.9$	0.973	$0.9909 \pm 0.0009$

<sup>a</sup> The uncertainties of *T* and *p* are 0.1 K and 0.05 MPa, respectively. Formation time of <sup>b</sup> 1 or <sup>c</sup> 3 h.



**Figure 2.** Fractionation factor  $\alpha_{H-V}$  as a function of formation temperature. Colored circles: this study; gray triangles: literature values [9].



**Figure 3.** Fractionation factor  $\alpha_{H-V}$  as a function of formation pressure. Light blue circles: 224.2–228.7 K; yellow circles: 243.2–243.3 K; pink circles: 262.9–263.1 K; open circles: other temperatures in this study; gray triangles: literature values [9].

Here, we discuss the possibility that the hydrogen isotope fractionation may decrease due to kinetic effects. The internal pressure of the pressure cell decreases slightly due to the formation of the methane hydrate. The average rate of the decrease in pressure  $\Delta P/\Delta t$  over 5 h was plotted as a function of the formation pressure (Figure 4). The  $\Delta P/\Delta t$  values are approximately -0.01 and -0.02 MPa h<sup>-1</sup> at 243.2–243.3 and 262.9–263.1 K, respectively. The rate of hydrate formation is independent of pressure and increases at high temperatures. Therefore, the increase in  $\alpha_{H-V}$  with increasing pressure (Figure 3) may be attributed to the increase in the formation pressure instead of the increase in  $\Delta P/\Delta t$ .



**Figure 4.** Average rate of the decrease in pressure ( $\Delta P/\Delta t$ ) over 5 h. Yellow circles: 243.2–243.3 K; pink circles: 262.9–263.1 K.

Hence, the hydrogen isotope fractionation of methane during methane hydrate formation clearly depends on the formation pressure. In conclusion, differences in the isotopic ratios of hydrate-bound methane and that surrounding the crystals yield temperature and pressure data regarding hydrate formation.

The isotopic ratios of hydrate-bound gases are useful not only in identifying gas sources, but also in evaluating the formation processes of naturally occurring gas hydrates [24–29]. Because isotopic fractionation of hydrogen in hydrocarbons occurs during gas hydrate formation, isotopic differences between the hydrate-bound gas and dissolved gas in pore water provide data for use in evaluating whether the current gas in the pore water is a contributor to the hydrate-bound gas, e.g., isotopic differences should be observed if the hydrates are formed and maintained, whereas no differences should be observed if they decompose [30–32]. Furthermore, an isotopic difference is useful in determining the environment wherein the hydrates were formed, because it yields data regarding the pressure at the time of hydrate formation. However, collecting the gas in the environment at the time of formation, along with the hydrate-bound gas, is necessary. The findings of this study are limited to pressures of <20 MPa and temperatures below the freezing point of water. Studies should be conducted under higher pressures and over wider temperature ranges to understand not only natural gas hydrates beneath the seafloor, but also methane hydrates that may occur on extraterrestrial planets [19,20] and their satellites [21–23]. Further studies regarding the effects of impurities (salinity), crystal size, and sediments on isotopic fractionation should also be conducted.

#### 3. Materials and Methods

The experimental systems and equipment used were the same as those used in our previous work [33], and the methane hydrates were synthesized in a pressure cell (internal volume: 42 mL) using research-grade methane (purity: 99.99%, Takachiho Chemical Industrial, Tokyo, Japan) as the guest gas. Fine ice powder (0.7 g) was placed in the cell, and the air within the cell was vacuumed at 77 K. An appropriate amount of methane was introduced into the cell, which was then immersed in a temperature-controlled liquid bath (243–268 K) or placed in a cold room (224–243 K). The methane trapped within the cell sublimated and reached the desired pressure at each temperature within 15 min. Hydrate formation was confirmed by a decrease in the pressure at the controlled temperature, and

the formation times were approximately 2 d, except for those of two samples used in verifying the kinetic effect (1 and 3 h at 263.0 K, Table 1). The temperature and pressure of the cell were measured using a thermistor (D617, Technol Seven, Tokyo, Japan) and pressure gauge (AP-14S, Keyence, Osaka, Japan), respectively, and the respective uncertainties of the temperature and pressure measurements were 0.1 K and 0.05 MPa.

Residual gas that was not encapsulated in the gas hydrate was collected while ensuring that the pressure was maintained above the equilibrium pressure of the methane hydrate. Subsequently, the cell was quenched at 77 K, and the hydrate sample was recovered. The hydrate was placed in a vacuum line, and liquid nitrogen and solid methane contaminating the hydrate samples were meticulously evaporated/sublimated using a vacuum pump. After verifying that the liquid nitrogen and solid methane were completely evaporated/sublimated by measuring the internal pressure of the vacuum line, the sample tube was heated to decompose the methane hydrate. Residual gas was introduced into a separate line, and the respective gas samples were collected using a gas-tight microsyringe.

Each gas was introduced into a continuous-flow isotope ratio mass spectrometer (Delta V Advantage, Thermo Fisher Scientific, Waltham, MA, USA) coupled with a gas chromatograph (TRACE GC Ultra, Thermo Fisher Scientific) equipped with a CP-PoraPLOT Q capillary column (length: 25 m, inner diameter: 0.32 mm, film thickness: 10  $\mu$ m, Agilent Technologies, Santa Clara, CA, USA). The hydrogen isotope compositions are reported as  $\delta$  values (‰).

$$\delta \ [\%] = \left(\frac{R_{sample} - R_{standard}}{R_{standard}}\right) \times 1000 \tag{1}$$

where *R* denotes the <sup>2</sup>H/<sup>1</sup>H ratio.  $\delta^2$ H is obtained by referring to the Vienna Standard Mean Ocean Water standards determined using National Institute of Standards and Technology RM8561 (NGS3), and the analytical precision is 0.6‰. The residual, hydrate-bound, original (initial), and standard gases were measured sequentially, and six measurements were performed for each gas sample to determine the mean and standard deviation of the stable isotope ratio of hydrogen.  $\alpha_{H-V}$  is defined as

$$\alpha_{\rm H-V} = \frac{R_{hydrate}}{R_{vapor}} \tag{2}$$

where  $R_{hydrate}$  and  $R_{vapor}$  denote the <sup>2</sup>H/<sup>1</sup>H ratios of the hydrate-bound and residual gases, respectively. As the methane hydrates are formed in a finite, closed system, the Rayleigh process [34] is applied, and the relationship between  $\alpha_{H-V}$  and the average isotope ratios of the hydrate-bound and residual gases is expressed as

$$\frac{\overline{R}_{hydrate}}{\overline{R}_{vapor}} = \frac{1 - f^{\alpha_{H-V}}}{(1 - f)f^{(\alpha_{H-V} - 1)}}$$
(3)

where  $\overline{R}_{hydrate}$  and  $\overline{R}_{vapor}$  denote the average <sup>2</sup>H/<sup>1</sup>H ratios of the hydrate-bound and residual gases, respectively, which are measured using a continuous-flow isotope ratio mass spectrometer. *f* is the fraction of residual methane gas within the cell, which is calculated using the decrease in pressure due to hydrate formation.

# 4. Conclusions

In this study, the hydrogen isotope compositions of residual and hydrate-bound gases were measured to understand the isotopic fractionation of methane between the gas and solid phases and collect data regarding the environments wherein hydrates form in nature. The  $\delta^2$ H of hydrate-bound methane formed below the freezing point of water was 5.7–10.3‰ lower than that of residual methane, indicating that methane hydrate generally encapsulates lighter molecules (CH<sub>4</sub>) instead of CH<sub>3</sub><sup>2</sup>H. The  $\alpha_{\text{H-V}}$  values between the gas and hydrate phases were in the range 0.9881–0.9932 at a temperature and pressure of 223.3–268.2 K and 1.7–19.5 MPa, respectively. Moreover,  $\alpha_{\text{H-V}}$  increased with the formation pressure but was primarily unaffected by temperature, suggesting that the difference in

the hydrogen isotopes of the hydrate-bound methane and surrounding methane yields data regarding the formation pressure. Accordingly, when hydrate-bound methane and environmental methane are obtained, the hydrogen isotope fractionation of methane during the formation of methane hydrate may be an indicator of the environment wherein the natural gas hydrates formed.

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