

# Hydrogen isotopic fractionation of methane at the formation of synthetic mixed-gas hydrate composed of methane and propane

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**ABSTRACT.** Hydrogen isotope fractionation for methane occurs between gas and hydrate phases at the formation of methane hydrate;  $\delta D$  of hydrate-bound methane is about 5‰ lower than that of residual methane. We suppose that the relation between the sizes of guest molecules and cage size of crystallographic structure affects the isotopic fractionation. Methane is enclathrated in both large and small cages of the structure I gas hydrate, therefore the isotopic difference is  $\delta D$  in mainly determined by molecules enclathrated in the large cages. On the other hand, in the case of methane and propane mixed-gas hydrate, methane prefers to be enclathrated in small cages, because propane is enclathrated only in the large cages of the structure II gas hydrate. In this study, we checked the effect of cage size on the hydrogen isotopic fractionation for methane by comparing pure methane hydrate and the mixed-gas hydrate composed of methane and propane. Synthetic gas hydrates were formed from fine ice powder and guest gases in a pressure cell. We retrieved residual and hydrate-bound gases and measured  $\delta D$  of methane by a CF-IRMS. The hydrogen isotopic differences between hydrate-bound and residual methane in the case of mixed-gas hydrate was smaller than those of pure methane hydrate reported by previous works, indicating that isotopic difference in methane  $\delta D$  for small cages is smaller than those for large cages.

**Keywords:** gas hydrate, methane, propane, isotopic fractionation, crystallographic structure

## 1. Introduction

Stable isotope fractionation of guest gas occurs during the formation of gas hydrates. In the case of methane hydrate, the hydrogen isotope ratio of the hydrate-bound methane is about 5 ‰ lower than that of the ambient methane (Hachikubo et al., 2007). This is consistent with the interpretation that the equilibrium pressure of  $CH_3D$  hydrate is slightly higher than that of  $CH_4$  hydrate (Ozeki et al., 2018) and  $CH_3D$  molecules are prone to be excluded from the hydrate phase. Recently, isotopic fractionation of propane hydrate has been investigated (Nikaido et al., 2018). The hydrogen isotope fractionation of propane occurs as well as methane, and the propane  $\delta D$  in the hydrate phase is about 4 ‰ smaller than that in the ambient gas.

The crystal structure of gas hydrate depends on the guest gas. Methane hydrate forms the structure I, composed of large and small cages ( $5^{12}6^2 : 5^{12} = 3 : 1$ ), whereas propane hydrate forms the structure II, composed of large and small cages ( $5^{12}6^4 : 5^{12} = 1 : 2$ ). Propane molecules can be engaged only in the large cages ( $5^{12}6^4$ ) due to the large guest size. However,

natural gas hydrates are mixed-gas hydrates. In the case of methane + propane system, the structure II forms under the influence of propane, and propane is selectively engaged in the large cages and the small cages are occupied by methane. Therefore, the formation of mixed-gas hydrate causes the segregation of guest molecules into large and small cages, and may affect the stable isotope fractionation. In this study, the hydrogen isotope fractionation of both methane and propane during the formation of methane and propane mixed-gas hydrate was investigated.

## 2. Material and methods

Methane (99.99% purity) and propane (99.99% purity) supplied by Takachiho Chemical Industrial were used as guest gases. A pressure cell (volume: 40 mL) was filled with 0.7 g of fine ice powder in a cold room (254 K). After vacuuming the air in the cell at the temperature of liquid nitrogen, the methane and propane were introduced and controlled their partial pressures at 274 K to avoid the formation of pure methane and propane hydrates. The partial pressure

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of propane was also controlled below the liquefaction pressure of propane. After the formation of mixed-gas hydrate, residual gas that was not engaged in the hydrate phase was collected. Hydrate crystals were sampled at the temperature of liquid nitrogen.

For the residual gas samples, the sample tube (container with valves) was connected directly to the vacuum line. The hydrate sample was dissociated directly in the vacuum line and the hydrate-bound gas was extracted. The composition of the hydrate-bound and residual gases were determined by a gas chromatograph (GC-2014, Shimadzu). The hydrogen isotope ratios of gas samples were determined by a stable isotope ratio mass spectrometer (CF-IRMS, DeltaV, Thermo Fisher Scientific). Stable isotope compositions are reported as  $\delta$  values (‰), and  $\delta D$  is given with reference to the V-SMOW standards.

### 3. Results and discussion

The difference in hydrogen isotope ratios ( $\delta D$  of residual gas –  $\delta D$  of hydrate-bound gas) is defined as  $\Delta\delta D$ . The  $\Delta\delta D$  values for methane and propane in their mixed-gas hydrate were  $3.1 \pm 1.0\text{‰}$  and  $5.5 \pm 1.3\text{‰}$ , respectively, whereas those of pure hydrate were reported to be  $4.8 \pm 0.4\text{‰}$  and  $4.4 \pm 0.4\text{‰}$  for methane and propane hydrates, respectively, according to the previous works (Hachikubo et al., 2007; Nikaido et al., 2018). There was no significant difference in propane  $\Delta\delta D$  between pure and mixed-gas hydrates. However, the methane  $\Delta\delta D$  of mixed-gas hydrate was slightly lower than that of pure methane hydrate.

When propane hydrate forms, propane molecules are engaged in the large cages of the structure II. Pure propane hydrate (Nikaido et al., 2018) and the methane + propane mixed-gas hydrate (this study) have the same crystallographic structure and the ratio of molecular size to the cage size is the same. Therefore, it can be explained that there is no difference in the hydrogen isotope fractionation of propane.

On the other hand, pure methane hydrate forms the structure I, and the contribution of large cages

is significant due to the ratio of the number of large to small cages (3 : 1) in the structure I. Therefore, methane in large cages mainly contributes to  $\Delta\delta D$  for pure methane hydrate ( $4.8 \pm 0.4\text{‰}$ ). In the case of methane in the mixed-gas hydrate of the structure II, methane is rather engaged in the small cages, because propane occupies large cages. Methane  $\Delta\delta D$  for mixed-gas hydrate ( $3.1 \pm 1.0\text{‰}$ ) is smaller than that of pure methane hydrate. These results indicate that the hydrogen isotope fractionation is smaller when methane is engaged in small cages of the structure II than when it is engaged in large cages of the structure I.

### 4. Conclusions

Since natural gas hydrate is a mixed gas system, methane and propane mixed gas hydrates were synthesized and the hydrogen isotope fractionation of both gases was investigated. In comparison with the previous works, the hydrogen isotope fractionation of methane was relatively small. As a result, the hydrogen isotope fractionation of methane is smaller when it is engaged in small cages of the structure II than in large cages of the structure I. In other words, the hydrogen isotope fractionation of the guest gas depends on the size ratio between the cage size and the guest gas.

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