



Isotopic fractionation of methane and ethane hydrates between gas and hydrate phases

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[1] Isotopic fractionation of carbon and hydrogen in methane and ethane during the formation of gas hydrates was investigated. The gas hydrate samples were experimentally prepared in a pressure cell and isotopic compositions of both residual and hydrate-bound gases were measured. δD of hydrate-bound molecules of methane and ethane hydrates was several per mil lower than that of residual gas molecules in the formation processes, while there was no difference in the case of $\delta^{13}C$. These isotopic differences in δD are enough small for discussing the source types of hydrate-bound gases using the $\delta^{13}C$ - δD diagram of Whiticar et al. [1986]. These results may provide useful insight into the formation process of gas hydrates.
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1. Introduction

[2] Gas hydrates are crystalline clathrate compounds composed of water and gas molecules that are stable at low temperature, high partial pressure of each gas component, and high gas concentration. Natural gas hydrates exist in permafrost and submarine/sublacustrine sediments at pressures (depths) greater than a few MPa. Since they are considered to be an unconventional energy resource and their guest gases act as greenhouse gases, the formation process of natural gas hydrates has been investigated by researchers. Sloan [1998] summarized the kinetics, phase equilibrium, thermodynamics, etc. of gas hydrates obtained from recent studies. The stable isotope ratio of natural gas hydrates seems to be useful in identifying their gas sources. Whiticar et al. [1986] proposed a genetic classification diagram for natural gas using $\delta^{13}C$ and δD of methane. It was expanded and defined as the $\delta^{13}C$ - δD diagram for the classification of methane sources [Whiticar, 1999]. In the diagram, large and small $\delta^{13}C$ values of methane indicate thermogenic and microbial origins, respectively, and δD of methane provides information on methyl-type fermentation or CO_2 reduction in the microbial region. Milkov [2005] constructed a global dataset of isotopic compositions of hydrate-bound gases and applied Whiticar's diagram to interpret gas origin. He showed that hydrate-bound methane is of thermogenic or microbial origin due to CO_2 reduction.

Recently, Kida et al. [2006] measured the isotopic composition of hydrate-bound gas obtained in Lake Baikal and concluded that it is of microbial origin due to methyl-type fermentation.

[3] On the other hand, isotopic fractionation occurs at a phase transition. The fractionation factor α between a host molecule of gas hydrate and liquid water has been reported by researchers. Davidson et al. [1983] first reported such fractionation of ^{18}O for tetrahydrofuran hydrate and showed that α is almost the same as that of an ice-liquid water system. Ussler and Paull [1995] showed the effect of ion exclusion and isotopic fractionation associated with gas hydrate formation. Maekawa and Imai [2000] and Maekawa [2004] revealed the isotopic fractionation of ^{18}O and D between methane hydrate and saline water under high pressure. These results indicate that gas hydrates enrich heavy isotopes of host molecules in their formation process and agree with the field observation that ^{18}O enrichment of pore water in marine sediments corresponds to low salinity, which is caused by dissociation of gas hydrates [Hesse and Harrison, 1981; Matsumoto, 2000; Matsumoto and Borowski, 2000].

[4] However, little attention has been paid to the isotopic fractionation between guest molecules of gas hydrate and gas bubbles/dissolved gas. From the viewpoint of mixed-gas hydrates, gas fractionation can occur between light and heavy guest molecules because the equilibrium pressures of their pure hydrates might differ from each other. If the difference in isotopic values between guest and residual gases is large, we need to apply Whiticar's diagram to the gas hydrate study with an appropriate correction. The aim of this work is to obtain fractionation factors for guest molecules in the formation of gas hydrates. Methane and ethane were used as guest gases since they are major components of natural gas hydrates. Measurements of isotopic compositions of carbon and hydrogen were obtained from the dissociated gas of synthetic hydrates and residual gas in a pressure cell after the formation of samples.

2. Experimental Apparatus, Materials, and Procedures

[5] Figure 1 shows a simplified schematic diagram of the experimental apparatus. Gas hydrate samples were formed in a cylindrical pressure cell made of stainless steel (volume capacity 120 ml). Temperature was measured with a platinum thermometer to an accuracy of ± 0.1 K and pressure with a pressure gauge having a resolution of 0.01 MPa. The cell was immersed in a temperature controlled liquid bath or placed in an insulated box in a cold room to maintain temperature with an accuracy of ± 0.1 K. A magnetic stirring

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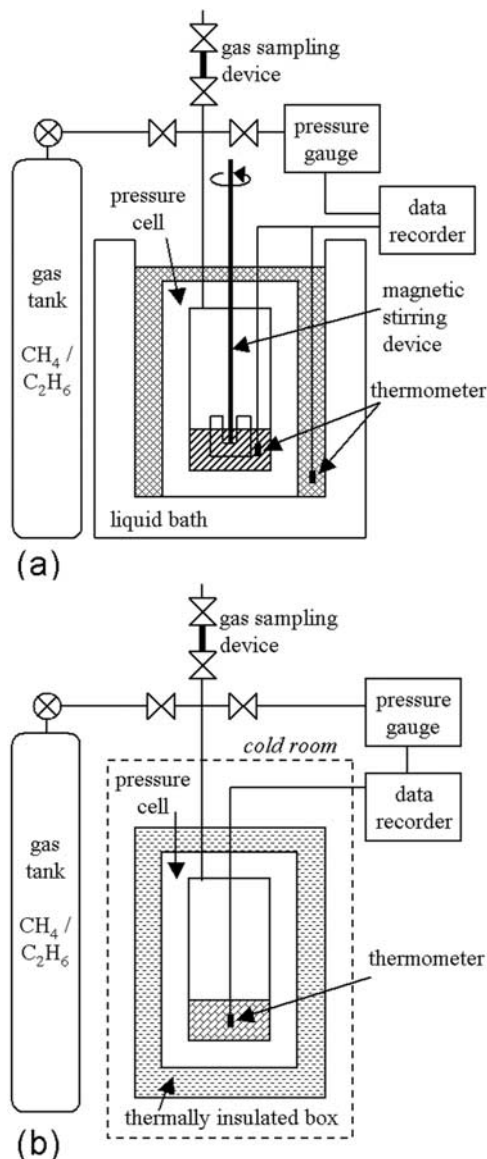


Figure 1. Schematic diagram of the experimental apparatus. (a) 274.2K. (b) Below the freezing point of water.

device agitated liquid water for enhancement of nucleation and mixing of gas and liquid phases at a temperature of 274.2 K. Fine ice powder was added to the cell without any agitation in experiments performed below the freezing point of water. Three kinds of gases were used in this study: gases A and B were methane with a purity of 99.999 mol% (Takachiho Chemical Industry Co. Ltd., Tokyo, Japan) and 99.9 mol% (Air Water Inc., Osaka, Japan), respectively. Gas C was ethane with a purity of 99.9 mol% again supplied by Takachiho Chemical Industry Co. Ltd. Liquid water was degassed and purified by distillation and deionization, and fine ice powder was prepared by shaving pure ice using a microtome. Liquid water or ice powder was placed in the cell and pressurized by the guest gases above their equilibrium pressures. The effect of gas consumption on the isotopic composition was investigated by changing the amount of liquid water or ice powder from 1 to 50 g. After the nucleation of gas hydrate, the pressure started to

decrease immediately and approached a steady-state value. The temperature was maintained for several days and then both phases of gas and hydrate were sampled to measure their isotopic compositions. For the isotopic analyses of carbon and hydrogen, a mass spectrometer (DELTA plus XP; Thermo Finnigan) was used. Isotopic compositions are reported as δ values defined as

$$\delta_{\text{sample}} = \left(\frac{R_{\text{sample}} - R_{\text{standard}}}{R_{\text{standard}}} \right) \times 1000(\text{‰}) \quad (1)$$

where R denotes the ratio of $^{13}\text{C}/^{12}\text{C}$ or D/H, and δ values, $\delta^{13}\text{C}$ and δD , are given with reference to the VPDB and VSMOW standards, respectively. The analytical precision of $\delta^{13}\text{C}$ is 0.1‰ and that of δD is 0.6‰. To check the effect of host molecules on δD of guest molecules, δD of water was also measured by the $\text{H}_2 - \text{H}_2\text{O}$ equilibrium method with VSMOW/SLAP calibration.

3. Results

[6] Results of isotopic measurements are shown in Table 1. Experiments were conducted in the temperature range 243.7 to 274.2 K and the initial pressure conditions ranged from 4.3 to 5.9 MPa (Gases A and B) and 2.3 to 2.4 MPa (Gas C). Gas hydrate and residual gas samples were collected about 1 day after their nucleation except for Sample Nos.1 and 2. We confirmed that the stabilized pressures were higher than the anticipated equilibrium pressures and no liquid water remained in the cell after the complete agitation at 274.2 K, except for Sample No.17. Gas hydrate in Sample No.17 was quickly separated from the residual water during the sampling procedure. Isotopic compositions of the three original gases and 20 sample gases were obtained and the results are plotted in Figure 2. Methane and ethane δD values in the hydrate phase were smaller than those in the gas phase, whereas their $\delta^{13}\text{C}$ values in the hydrate phase were almost the same as those in the gas phase. These results indicate that the heavy molecules, CH_3D and $\text{C}_2\text{H}_5\text{D}$, are poorly encaged in the hydrate although the behavior of $^{13}\text{CH}_4$ and $^{13}\text{C}^{12}\text{CH}_6$ seems to be the same as that of the light molecules ($^{12}\text{CH}_4$ and $^{12}\text{C}_2\text{H}_6$).

[7] In Figure 2a, δD of the residual gas increased compared to that of the original gas because CH_3D seemed to remain in the gas phase and light molecules concentrated in the hydrate phase. δD values of both phases in Sample No.14 were larger than those in other samples (Nos.12, 13, 15 and 16) according to a Rayleigh process because the amount of ice powder was relatively large (35 g). Gas sample Nos.1 and 2 in Table 1 were retrieved from the pressure cell about 3 h and 4 days after their nucleation, respectively. The hydrate phase δD of Sample No.1 was larger than those of the other samples at 274.2 K because of insufficient isotopic equilibrium. Since the values of Sample Nos.2–7 were almost the same ($-178.1 \pm 0.3\text{‰}$ VSMOW), a formation time of one day is sufficient to reach the same isotopic fractionation as the case of four days in this closed system. In addition, δD values of the guest molecules of Sample Nos.2–7 provided almost the same isotopic results while those of the host H_2O molecules were different from each other (No.4: $+0.9\text{‰}$ VSMOW, No.5: -288.7‰ VSMOW, and Nos.2, 3, 6, 7: -73.7‰ VSMOW, respec-

Table 1. Isotopic Compositions and Their Standard Deviations for Residual Gas and Hydrate-Bound Gas

Sample Gas	Temp, K	Pressure, MPa		Water, g	Gas Phase		Hydrate Phase		Difference	
		Initial	Final		$\delta^{13}\text{C}$, ‰	δD , ‰	$\delta^{13}\text{C}$, ‰	δD , ‰	$\delta^{13}\text{C}$	δD
Gas A (original)					-41.4 ± 0.1	-174.8 ± 0.7				
Gas B (original)					-66.2 ± 0.2	-177.6 ± 1.3				
Gas C (original)					-28.7 ± 0.1	-260.1 ± 0.8				
No.1 Gas A ^a	274.2	4.9	3.9	10	-41.1 ± 0.0	-173.8 ± 0.2	-41.4 ± 0.1	-176.4 ± 0.2	0.2	2.6
No.2 Gas A ^b	274.2	4.8	3.9	10	-41.4 ± 0.1	-173.5 ± 0.6	-41.3 ± 0.1	-178.2 ± 0.8	0.0	4.7
No.3 Gas A	274.2	5.2	3.9	10	-41.4 ± 0.1	-172.3 ± 0.5	-41.4 ± 0.0	-177.8 ± 0.7	-0.1	5.5
No.4 Gas A ^c	274.2	5.1	4.0	10	-41.3 ± 0.0	-173.2 ± 0.5	-41.5 ± 0.1	-177.9 ± 0.4	0.2	4.7
No.5 Gas A ^d	274.2	5.0	3.9	10	-41.4 ± 0.0	-173.4 ± 0.2	-41.4 ± 0.1	-178.1 ± 0.2	0.0	4.6
No.6 Gas A	274.2	5.2	4.6	5	-41.3 ± 0.1	-173.1 ± 0.7	-41.3 ± 0.1	-178.0 ± 1.1	0.0	5.0
No.7 Gas A	274.2	5.3	4.8	3	-41.3 ± 0.1	-174.4 ± 0.6	-41.6 ± 0.2	-178.7 ± 0.3	0.2	4.2
No.8 Gas A	265.2	4.5	3.6	10	-41.4 ± 0.1	-171.7 ± 0.6	-41.3 ± 0.0	-181.3 ± 0.6	-0.1	9.5
No.9 Gas A	254.6	4.3	3.3	10	-41.4 ± 0.1	-171.8 ± 0.6	-41.5 ± 0.1	-180.2 ± 0.6	0.1	8.4
No.10 Gas A	254.6	5.7	5.5	1	-41.4 ± 0.2	-174.2 ± 0.7	-41.8 ± 0.2	-182.1 ± 1.0	0.4	7.9
No.11 Gas A	243.7	—	—	10	-41.4 ± 0.1	-172.9 ± 0.6	-41.4 ± 0.1	-183.6 ± 0.5	0.0	10.7
No.12 Gas B	265.2	5.0	4.1	10	-66.2 ± 0.1	-174.6 ± 0.4	-66.1 ± 0.1	-183.2 ± 0.9	-0.1	8.6
No.13 Gas B	254.6	5.0	4.1	10	-66.4 ± 0.1	-173.9 ± 0.5	-66.3 ± 0.1	-182.8 ± 0.8	-0.1	8.9
No.14 Gas B	254.6	—	—	35	—	-172.0 ± 0.2	—	-180.4 ± 0.9	—	8.4
No.15 Gas B	254.6	5.9	5.0	10	-66.2 ± 0.1	-176.4 ± 0.2	-66.0 ± 0.2	-185.2 ± 0.4	-0.2	8.8
No.16 Gas B	254.6	5.8	5.6	3	—	-175.6 ± 0.5	-66.0 ± 0.1	-185.3 ± 0.5	—	9.7
No.17 Gas C	274.2	2.4	0.6	50	-28.7 ± 0.1	-260.3 ± 0.2	-28.7 ± 0.0	-260.9 ± 0.4	0.0	0.6
No.18 Gas C	274.2	2.4	2.0	10	-28.7 ± 0.1	-260.7 ± 0.5	-28.7 ± 0.0	-261.2 ± 0.4	0.1	0.5
No.19 Gas C	274.2	2.4	2.0	5	-28.7 ± 0.1	-259.7 ± 0.4	-28.7 ± 0.0	-261.4 ± 0.4	0.0	1.8
No.20 Gas C	274.2	2.3	2.0	3	-28.6 ± 0.0	-260.2 ± 0.6	-28.7 ± 0.0	-261.8 ± 0.5	0.1	1.6

^aFormation time was 3 h.^bFormation time was 4 days.^c δD of host molecules was +0.9‰ VSMOW.^d δD of host molecules was -288.7‰ VSMOW.

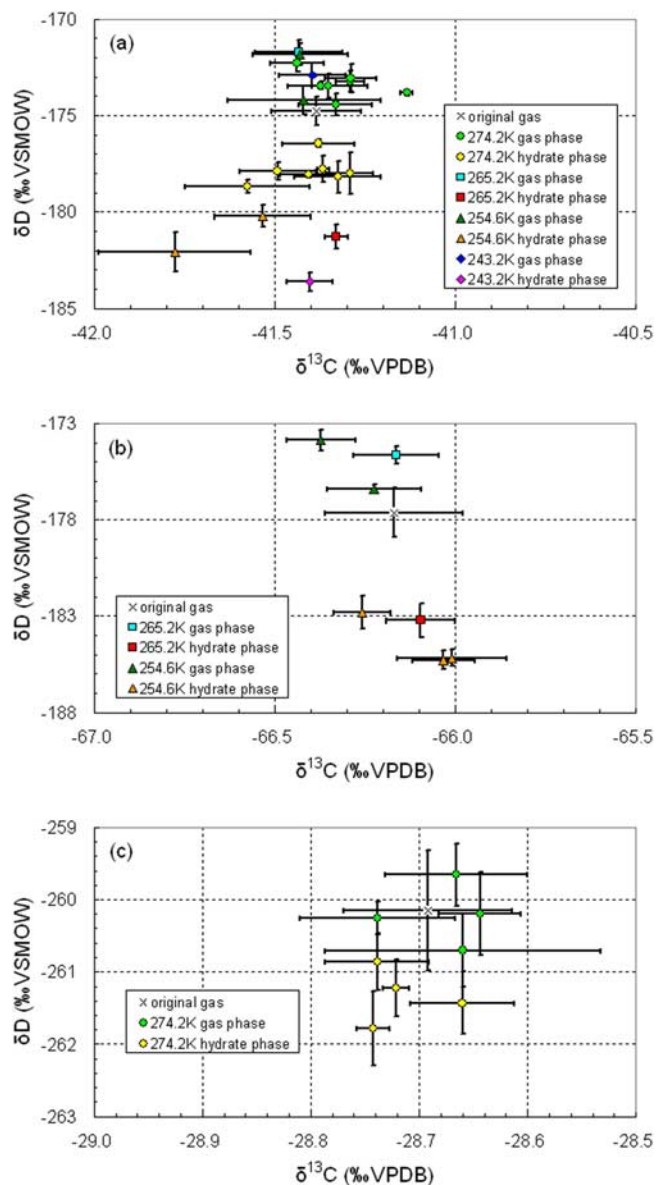


Figure 2. δD and $\delta^{13}C$ distributions in residual, hydrate-bound, and original gases for (a) methane hydrate (gas A), (b) methane hydrate (gas B), and (c) ethane hydrate (gas C).

tively). It is possible that the host molecules did not cause the above-mentioned isotopic differences in δD . Figures 2b and 2c show δD plotted against $\delta^{13}C$ in cases of methane (gas B) and ethane (gas C) hydrates, respectively. Even with different $\delta^{13}C$ values of methane, δD of the hydrate phase was smaller than that of the gas phase as seen in Figure 2a. Although the difference in ethane δD between the two phases was $1.1 \pm 0.7\text{‰}$, which is smaller than that of methane δD , we can say that isotopic fractionation of guest gas also exists in the formation of ethane hydrate, as well as methane hydrate.

[8] Figure 3 shows $\Delta\delta D$, which is defined as the difference in δD between the gas and hydrate phases, plotted against the formation temperature. $\Delta\delta D$ was $9.0 \pm 0.9\text{‰}$ and $4.8 \pm 0.4\text{‰}$ when methane hydrate was prepared from ice powder and liquid water, respectively. $\Delta\delta D$ for ethane

hydrate was relatively small as mentioned above. The fractionation factor α between a guest molecule of hydrate and residual gas is simply expressed as

$$\alpha = \frac{R_{\text{hydrate}}}{R_{\text{gas}}} \quad (2)$$

The fractionation factors α obtained were 0.9893 ± 0.0008 and 0.9942 ± 0.0004 when methane hydrate was prepared from ice powder and liquid water, respectively, and 0.9985 ± 0.0009 when ethane hydrate was prepared from liquid water. How methane hydrates are formed from ice powder with a larger difference in δD remains an open question. In their diagram, Whiticar *et al.* [1986] showed that the field of microbial origin produced by acetate-type fermentation ranged from -400 to -250‰ in δD and CO_2 reduction ranged from -250 to -170‰ in δD . It can be concluded that we can safely apply Whiticar's $\delta^{13}C$ - δD diagram to discuss the source types of hydrate-bound gas as has been done by Milkov [2005], because the isotopic difference in δD obtained in this study (less than 10‰) seems too small.

4. Concluding Remarks

[9] The δD value of guest molecules of methane and ethane hydrates was smaller than that of residual gas molecules in their formation processes. The difference in δD between the gas and hydrate phases obtained in this study was $9.0 \pm 0.9\text{‰}$ and $4.8 \pm 0.4\text{‰}$ for methane hydrate prepared from ice powder and liquid water, respectively, and 1.1‰ for ethane hydrate, whereas that of $\delta^{13}C$ was zero or small. This is the first report to reveal the isotopic fractionation of guest gas molecules in the formation of gas hydrates. It is confirmed that isotopic fractionation is enough small for discussing the gas origin of natural gas hydrates because the difference between both phases is relatively small. In addition, an isotopic difference between hydrate-bound and surrounding gases revealed in sediment core analysis can provide information to discuss when the gas hydrate formed. For example, we can infer from the difference in $\delta^{13}C$ between hydrate-bound and surrounding gases that a massive gas hydrate was not formed recently. Although natural gas hydrates exist in submarine/sublacustrine sediments together with pore water in which the gas

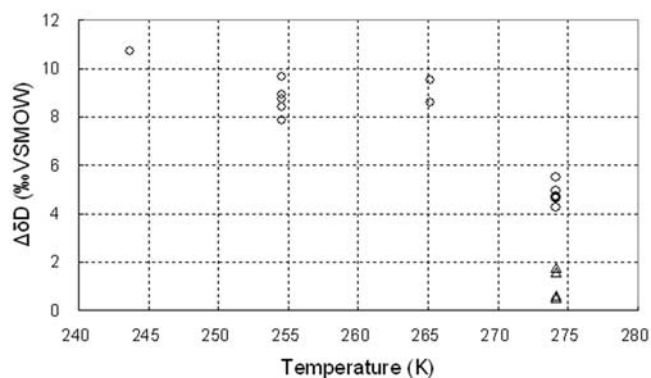


Figure 3. Effect of temperature on δD difference between residual and hydrate-bound gases. Open circles, methane hydrate; triangles, ethane hydrate.

dissolves well under high partial pressure, we have no definite information on isotopic data of dissolved gas in water. Obtaining an isotopic composition between the three phases (gas, hydrate and dissolved gas in water) simultaneously will be the subject of a future study. Further studies on the effects of temperature, pressure, impurities (salinity), crystal size, and formation rate on the process of isotopic fractionation are also needed.

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