

Experimental study on isotopic fractionation in water during gas hydrate formation

TATSUO MAEKAWA*

Institute for Geo-Resources and Environment, National Institute of Advanced Industrial Science and Technology, AIST Tsukuba Central 7, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8567, Japan

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Isotopic fractionation of oxygen and hydrogen in water caused by gas hydrate formation was investigated experimentally. Two different gas hydrates in structures, Structure I hydrate and Structure II hydrate, were formed with methane and krypton gases in a NaCl solution. Isotopic fractionation during gas hydrate formation was observed by measuring oxygen and hydrogen isotopic compositions in the solutions sampled before and after gas hydrate formation. Heavy isotopes of oxygen and hydrogen in water were depleted in the solution resulting from that those isotopes were concentrated in the gas hydrate. The isotopic fractionation was larger as increasing amounts of gas hydrates that were calculated from both the decrease of gas pressure and increase of NaCl concentration in solution. The isotopic fractionation factors of oxygen and hydrogen in water between gas hydrate and liquid water were determined to be 1.0023–1.0032 and 1.014–1.022, respectively. The significant difference of the gas hydrate structures was not observed beyond the analytical errors. These factors are similar to those between ice and liquid water.

Keywords: gas hydrate, methane hydrate, clathrate hydrate, isotopic fractionation, fractionation factor

INTRODUCTION

Natural gas hydrates occur in sediment under specific conditions of high pressure and low temperature that are present in permafrost regions and beneath the sea floor in continental margins. These gas hydrates are of societal concern as a potential energy resource and a source for atmospheric methane associated with global warming because they contain large amounts of natural gas that are mainly composed of methane (Kvenvolden, 1988).

Gas hydrate is an ice-like crystalline solid and a kind of clathrate compound in which gas molecules are held within rigid cages of water molecules. Gas hydrates normally form in a crystal structure of Structure I, Structure II or Structure H (Sloan, 1998). The structure of gas hydrate depends on the molecular size of gases included in the structure. Structure I hydrate has a body-centered cubic lattice and is stabilized by gas molecules such as methane, ethane, carbon dioxide and xenon. The Structure I hydrates with biogenic gases containing mostly methane are found in permafrost and deep-sea sediments (Matsumoto *et al.*, 2000; Kvenvolden and Kastner, 1990; Brooks *et al.*, 1991; Ginsburg *et al.*, 1993). Structure II

hydrate has a diamond lattice and forms with propane and iso-butane. The hydrates with thermogenic gases containing hydrocarbons are found in sediments in the Gulf of Mexico and the Caspian Sea (Brooks *et al.*, 1984; Sassen *et al.*, 1999; Ginsburg *et al.*, 1992). Krypton and argon gases also stabilize Structure II hydrates (Sloan, 1998). Structure H hydrate has a hexagonal lattice and is suggested to occur naturally in the Gulf of Mexico (Sassen and MacDonald, 1994).

In deep-sea sediments that contain natural gas hydrates, heavy oxygen and hydrogen isotope enrichment are observed in the pore water associated with lowered concentration of dissolved salts (Hesse and Harrison, 1981; Matsumoto, 2000). The reason is the pore water was diluted in the sampling process by the water released from natural gas hydrates that were enriched in heavy oxygen and hydrogen isotopes in water with low salinity. The enrichment of a heavy oxygen isotope in pore water was used to estimate the amount of *in situ* natural gas hydrate, as well as the decrease of chloride concentration (Matsumoto, 2000; Matsumoto and Borowski, 2000). However, there are few experimental studies on the isotopic fractionation of oxygen in water during gas hydrate formation. Moreover, the isotopic fractionation factor of hydrogen in water between gas hydrate and liquid water has never been reported, except for the preliminary results of Structure I hydrate by Maekawa and Imai (2000).

The object of this work is to determine the isotopic

*E-mail address: tatsuo-maekawa@aist.go.jp

fractionation factors of oxygen and hydrogen in water during the formation of Structure I and Structure II hydrates by laboratory experiments. In these hydrates, each water molecule consisting of a rigid three-dimensional framework lattice is hydrogen-bonded to its four nearest neighbors. On the other hand, hydrophobic gases such as rare gases and light hydrocarbon gases are physically enclosed by hydrogen-bonded water molecules without strong attractive forces (Davidson, 1973). In the case of hydrophobic gases, the interaction between enclosed gas and water is suggested to be weaker than that between hydrogen-bonded water molecules (Jeffrey and McMullan, 1967). Therefore, the isotopic fractionation in water during gas hydrate formation primarily depends on the interaction between hydrogen-bonded water molecules in the hydrate lattice.

In this work, methane and krypton gases were used to form Structure I and Structure II hydrates, respectively. In the case of hydrogen isotopes in a methane hydrate, the isotopic partition of hydrogen between water and methane is also considered. However, the isotopic fractionation is neglected assuming that the amount of hydrogen isotopes in water is much larger than that in methane in liquid and methane gases were entrapped into a gas hydrate lattice without equilibration with water. Structure II hydrate naturally forms with hydrocarbons such as propane. However, since this kind of gases is suggested to rarely affect isotopic fractionation in water, I

used krypton to form Structure II hydrates because of its advantages of no isotopic exchanges with water and no liquefaction at high pressure.

EXPERIMENTAL APPARATUS

The experimental apparatus used in this work consists of a cylindrical high-pressure cell immersed in a glycol-water bath in which temperature is controlled by a cooling unit (Fig. 1). This high-pressure stainless steel cell has an available volume of 705 ml. Platinum resistance thermometers and a pressure transducer are connected to the cell to measure temperature and pressure inside the cell. The accuracies of temperature and pressure measurements are ± 0.2 K and ± 0.05 MPa, respectively. A magnetic stirring mixer agitates liquid in the cell for accelerating gas hydrate formation. Two glass windows are placed on the upper side of the cell for visual observation. The cell has an outlet with a metal filter at the bottom through which the solution in the cell can be taken out under high pressure.

EXPERIMENTAL PROCEDURE

Structure I and Structure II hydrates were formed from research-grade methane and krypton gases, respectively, with a liquid solution containing different concentrations of NaCl. The change in the NaCl concentration of the

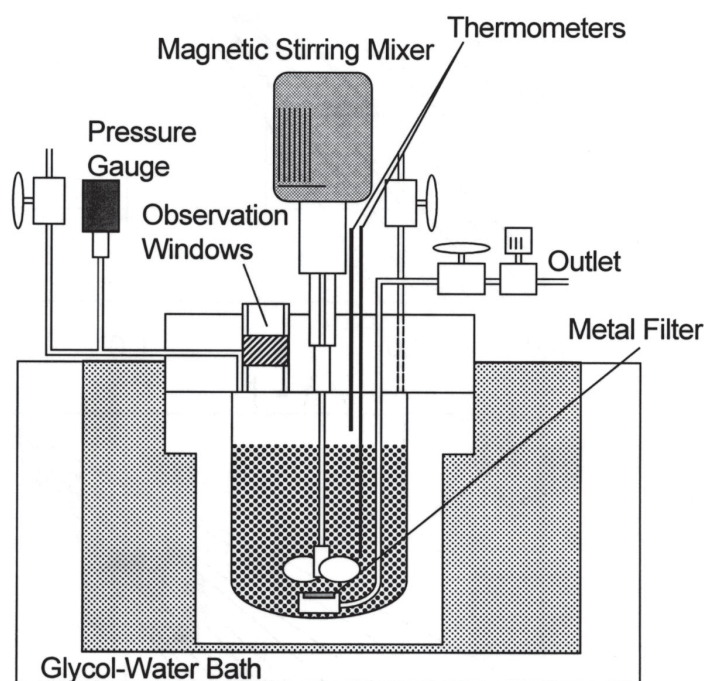


Fig. 1. Schematic diagram of experimental apparatus.

solution during gas hydrate formation was necessary to estimate the amount of gas hydrate, as described in the following section. However, it is possible that the experimental results with a very low NaCl solution can be regarded as the same as those with pure water. The solutions used in this work contained 0.003 wt% to 3.0 wt% NaCl. A series of NaCl solutions were prepared by dissolving research-grade NaCl salts in distilled waters of which isotopic compositions were about -5% and -30% for $\delta^{18}\text{O}$ and δD values, respectively. The research-grade gases were supplied by Takachiho Chemical Industry Corporation and Nippon Sanso Corporation.

First, 250 to 450 ml of a NaCl solution was charged into the cell, and the cell was placed in a glycol-water bath after sealing the lid. The cell was repeatedly flushed with methane or krypton from a gas cylinder. The pressurized gas was introduced into the cell to the desired pressure and sealed by closing the gas valves. After equilibration with the solution at room temperature, the initial solution before gas hydrate formation was sampled through the outlet at the bottom of the cell. After lowering the temperature of the solution to 273.5 K or 283.5 K, gas hydrate formation was induced by increasing the stirring rate of the magnetic mixer. Gas hydrate formation was confirmed by visual observation through the windows on the upper side of the cell. While gas hydrate formed at constant temperature, gas pressure decreased to the equilibrium pressure because gas hydrate trapped the gas molecules in vapor into the lattice. The equilibrium pressures of methane hydrates at 273.5 K are 2.72 MPa with pure water, 3.06 MPa with a 3.0 wt% NaCl solution and 3.26 MPa with a 4.5 wt% NaCl solution. The equilibrium pressure at 283.5 K is 7.20 MPa with pure water (Sloan, 1998). For the krypton hydrate, Holder *et al.* (1980) experimentally determined the equilibrium pressure at 273.2 K is 1.47 MPa with pure water. The equilibrium pressure of krypton hydrate at the formation temperature of 273.5 K used in this work is suggested to be slightly higher than that at 273.2 K. The solution was intermittently sampled through the outlet before the gas pressure reached the equilibrium pressure. The solutions sampled before and after gas hydrate formation were measured for NaCl concentrations and isotopic compositions of oxygen and hydrogen in waters.

ANALYTICAL METHOD

Oxygen and hydrogen isotope ratios of waters in sampled solutions were determined with a mass spectrometer using the equilibrium technique. In the case of oxygen isotopic measurement, a certain volume of the solution was added to a glass flask, degassed and equilibrated with CO_2 standard gas provided from a gas cylinder. The flask was shaken in a water bath at constant temperature for

five hours to complete the isotopic exchange. Then, the oxygen isotopic ratio of the equilibrated CO_2 gas was determined using a Finnigan delta S mass spectrometer. For hydrogen isotopic measurement, the solution was equilibrated with H_2 standard gas, and the hydrogen isotopic ratio of the H_2 gas was determined after equilibration. Since dissolved NaCl affects hydrogen isotope partitioning between its solution and H_2 gas, the isotopic ratios of hydrogen obtained by the equilibrium method were revised with the equation of the isotope salt effect on hydrogen isotopic partition which was proposed by Horita *et al.* (1993). These isotopic compositions are expressed in conventional delta notation in per-mil relative to the SMOW standard. The precision of the isotopic analysis is $\pm 0.1\%$ and $\pm 1\%$ for $\delta^{18}\text{O}$ and δD values, respectively. The NaCl concentrations of the sampled solutions were measured using an ion chromatograph (Shimadzu PIA-1000).

ESTIMATION OF FRACTIONATION FACTOR

Two different processes of isotopic partition between gas hydrate and NaCl solution during gas hydrate formation were considered in this work: batch-type isotopic fractionation and Rayleigh-type isotopic fractionation. Assuming that entire gas hydrate was in equilibrium with the solution throughout gas hydrate formation when each of them was isotopically homogeneous, the fractionation factor α is calculated from

$$\ln \frac{R}{R_0} = -(\alpha - 1) \cdot (1 - f): \text{Batch-type fractionation} \quad (1)$$

where R is the isotopic ratio of $^{18}\text{O}/^{16}\text{O}$ or D/H of water in the solution and R_0 is this ratio in the initial solution before gas hydrate formation. The f value is defined as the ratio of water molecules in the solution to those in the initial solution.

$$f = \frac{N_{\text{liquid}}}{N_0} = 1 - \frac{N_{\text{hydrate}}}{N_0} \quad (2)$$

where N_{liquid} , N_{hydrate} and N_0 are the numbers of water molecules in the solution, gas hydrate and initial solution before gas hydrate formation, respectively. Using delta notation, the equation of batch-type fractionation is changed to

$$\Delta\delta = \delta - \delta_0 = -1000 \cdot (\alpha - 1) \cdot (1 - f) \quad (3)$$

where δ is the isotopic composition expressed in delta notation in per mil of $\delta^{18}\text{O}$ or δD of water in solution,

and δ_0 is that in the initial solution before gas hydrate formation.

On the other hand, assuming that the solution is equilibrated with only the surface layer of gas hydrate crystals and isotopic values of gas hydrate were left as the original values of its formation time, the formation factor α is calculated from

$$\ln \frac{R}{R_0} = (\alpha - 1) \ln f: \text{Rayleigh - type fractionation.} \quad (4)$$

This situation is analogous to a Rayleigh distillation. Using delta notation, the equation of Rayleigh-type fractionation is changed to

$$\Delta\delta = \delta - \delta_0 = 1000 \cdot (\alpha - 1) \ln f. \quad (5)$$

The $\Delta\delta$ value and f value are necessary for estimation of the fractionation factor α according to the equations. The $\Delta\delta$ value is obtained by measurement of isotopic compositions of water in both solutions sampled before and af-

ter gas hydrate formation in each experiment. The f value, however, cannot be directly obtained because gas hydrate easily dissociates in the sampling process from the high-pressure cell. The f values in each experiment are estimated from both the decrease of gas pressure and increase of NaCl concentration in solution during gas hydrate formation.

At first, the f value is calculated by the decrease of gas pressure in vapor (f_{GasPres}). Gas hydrates entrap gas molecules into their lattice during their formation, resulting in a decrease of gas pressure. The amount of gas molecules can be obtained by the pressure difference between before and after gas hydrate formation. In this work, the amount of gas molecules in vapor was calculated using Soave-Redrich-Kwong equation of state (Soave, 1972), densities of gas hydrate and solution, and gas solubilities in solutions. The solubilities of methane and krypton in liquid water were calculated by Krichevsky-Kasarnovsky equation with Henry's constants for methane (Rettich *et al.*, 1981) and krypton (Yaws *et al.*, 1999), partial molar volume of gases at infinite dilution (Rettich *et al.*, 1981; Moore *et al.*, 1982) and salting-out coefficient for meth-

Table 1. NaCl concentrations and isotopic compositions of oxygen and hydrogen in water in solution during gas hydrate formation. P_0 : initial pressure, P : final pressure, C_0 : NaCl concentration of the initial solution, C : NaCl concentration of the residual solution after gas hydrate formation. The results of runs 1–5 of Structure I hydrate were already reported in Maekawa and Imai (2000).

Run	T [K]	P_0 [MPa]	P [MPa]	C_0 [wt%]	C/C_0	$\Delta\delta^{18}\text{O}$ [‰]	$\Delta\delta\text{D}$ [‰]
<i>Structure I hydrate (Methane hydrate)</i>							
1.	273.5	8.42	3.81	3.55	1.26	−0.66	−3.7
2.	273.5	6.73	3.50	3.47	1.27	−0.67	−4.8
3.	273.5	5.40	3.60	3.29	1.25	−0.64	−3.7
4.	273.5	9.15	3.92	3.04	1.45	−0.95	−6.8
5.	273.5	8.92	4.37	3.02	1.53	−0.99	−7.2
6.	273.5	8.50	3.30	3.00	1.47	−0.92	−7.0
7.	273.5	7.35	3.44	0.102	1.21	−0.49	−3.0
8.	273.5	4.38	2.92	0.095	1.22	−0.40	−2.7
9.	273.5	7.58	3.00	0.101	1.50	−0.90	−5.8
10.	273.5	8.35	3.47	0.00251	1.35	−0.69	−4.7
11.	273.5	7.10	4.74	0.00237	1.32	−0.67	−3.6
12.	273.5	4.33	6.78	0.00323	1.26	−0.55	−4.0
13.	273.5	5.08	7.18	0.00298	1.50	−0.96	−5.3
14.	283.5	12.00	7.80	0.00344	1.41	−0.92	−5.1
15.	283.5	10.70	7.90	0.00312	1.51	−1.00	−5.4
<i>Structure II hydrate (Krypton hydrate)</i>							
1.	273.5	3.72	1.85	0.00326	1.18	−0.47	−3.2
2.	273.5	3.57	1.50	0.00371	1.13	−0.30	−2.1
3.	273.5	3.52	2.02	0.00367	1.15	−0.38	−2.1
4.	273.5	4.28	1.50	0.00345	1.19	−0.43	−2.9
5.	273.5	3.25	1.60	0.00334	1.19	−0.48	−2.5
6.	273.5	4.10	1.62	0.00338	1.26	−0.58	−4.0
7.	273.5	2.90	1.60	0.00301	1.41	−0.78	−5.8

ane solubility (Cramer, 1984). The number of water molecules in gas hydrate, N_{hydrate} , is calculated using the number of water molecules per gas molecules, hydration number (n):

$$N_{\text{hydrate}} = n \cdot \Delta N_{\text{Gas}} \quad (6)$$

where ΔN_{Gas} is the difference of the amount of gas molecules in vapor between before and after gas hydrate formation. The hydration number is 5.75 in Structure I hydrate and 5.67 in Structure II hydrate when all cages in the hydrate lattice are completely occupied by gas molecules. However, the actual hydration number is suggested to be larger than that when assuming full occupancies of all cages because some cages in the hydrate lattice are vacant of gas molecules (Sloan, 1998). The larger hydration number leads to a larger amount of gas hydrates formed. Therefore, the f_{GasPres} value obtained from the minimum hydration number assumed by full occupancies is suggested to be the maximum value.

On the other hand, the f value can be also estimated from the increase of NaCl concentration in solution during gas hydrate formation (f_{NaCl}). The NaCl concentration in solution increases as gas hydrate formation proceeds because gas hydrate crystals expelled dissolved salt from their lattices into the residual solution. Assuming gas hydrates have no salts in their lattice, the f value can be calculated by the following equation,

$$f_{\text{NaCl}} = \frac{C_0 \cdot (100 - C)}{C \cdot (100 - C_0)} \quad (7)$$

where C_0 and C are the NaCl concentrations in wt% in solutions before and after gas hydrate formation, respectively. In actual experiments, part of the solution is suggested to be entrapped as liquid inclusions surrounded by aggregates of gas hydrate crystals. These inclusions entrapped in gas hydrate aggregates are isolated from the residual solution in which the salt concentration continues to increase as gas hydrate formation proceeds. After isolation, gas hydrate is suggested to be difficult to form continuously in their inclusions because of a lack of gas molecules in the inclusions. Even if gas hydrates form in inclusions, the salt concentration of an isolated inclusion is suggested to remain lower than that in residual solution because gas hydrate is difficult to form in the solution having a higher concentration of NaCl. Consequently, the dissolved salt in residual solution is excessively concentrated, leading to an overestimation on the amount of gas hydrate (N_{hydrate}). Therefore, the f_{NaCl} value obtained by using the equation leads to the minimum value.

The range of f value in each experiment is limited between values obtained from the decrease of gas pres-

sure and increase of NaCl concentration in solution during gas hydrate formation.

RESULTS

The formation of 15 Structure I hydrates with methane and seven Structure II hydrates with krypton was carried out in this work. The NaCl concentrations and isotopic compositions of oxygen and hydrogen of water in solutions sampled before and after gas hydrate formation were measured in each experiment. These results are tabulated in Table 1. The experimental results show that the NaCl concentration in solution was increased and heavy isotopes of oxygen and hydrogen in water were depleted after gas hydrate formation, which suggests that gas hydrates expelled dissolved salt into the solution and concentrated heavy isotopes of water in their lattice.

These results are shown in Figs. 2 to 4. The result in each experiment is represented as a bar with the lateral width indicating the range of f values estimated from both the gas pressure decrease in vapor (f_{GasPres}) and NaCl concentration increase in solution (f_{NaCl}). The figures show that the differences of isotopic compositions in water between before and after gas hydrate formation are larger as the amount of gas hydrate increases. Several lines and curves represent the variations of the difference of isotopic compositions at a specific fractionation factor calculated by the equation of fractionation. Dotted lines indicate the expected isotopic changes when a batch-type isotopic fractionation occurred and solid curves indicate these changes when a Rayleigh-type isotopic fractionation occurred.

The isotopic fractionation factors in water between gas hydrate and liquid solution are estimated by the least-square fitting method using experimental data. The regression results are in Table 2. The regressions were carried out with the experimental data classified by experimental conditions of hydrate structure, salt concentration and formation temperature. In each experimental condition, both formation processes of batch-type and Rayleigh-type fractionations are considered. The fractionation factors estimated from using f_{GasPres} and f_{NaCl} are represented as α_{GasPres} and α_{NaCl} , respectively, and the fractionation factor obtained from actual experiments is between these values. Considering both formation processes of batch-type and Rayleigh-type fractionations, the fractionation factors between Structure I hydrate and liquid water containing less than 0.2 wt% NaCl at the formation temperature of 273.5 K are estimated to be 1.0023–1.0032 for oxygen isotopes and 1.014–1.019 for hydrogen isotopes. Following this estimation, the isotopic fractionation factors of oxygen and hydrogen between Structure I hydrate and saline solution containing more than 3 wt% NaCl at 273.5 K are estimated to be 1.0024–1.0034 and 1.017–

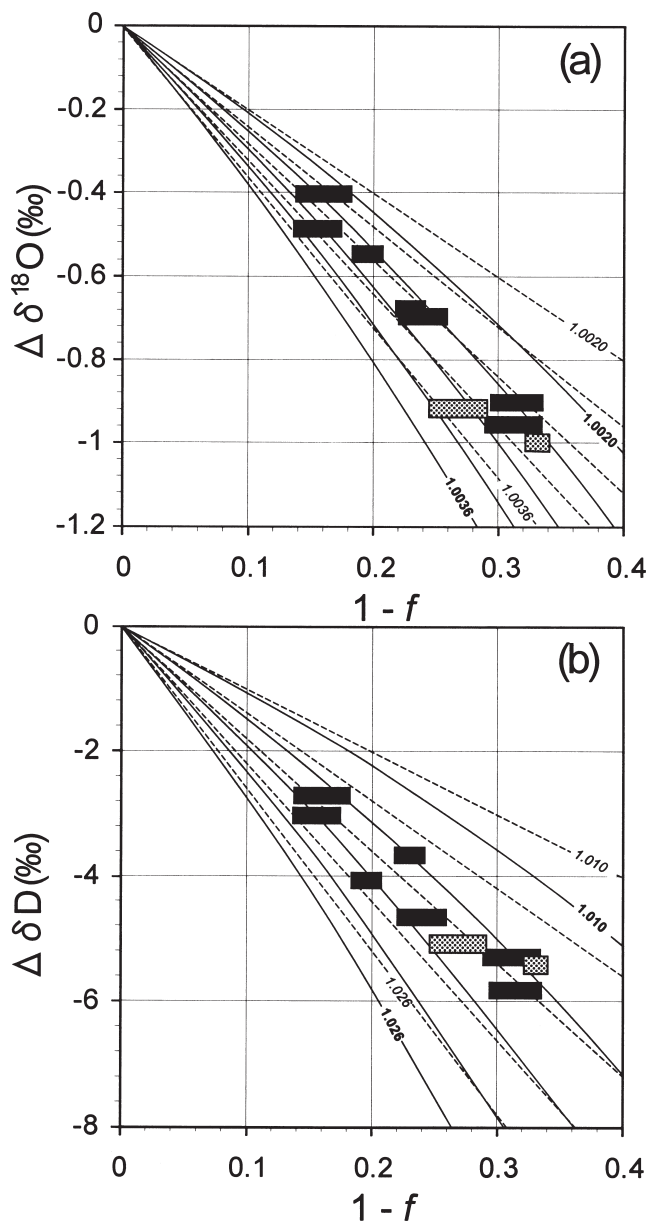


Fig. 2. Results of isotopic fractionation of oxygen (a) and hydrogen (b) in water when Structure I hydrate formed in water containing less than 0.2 wt% NaCl. Each result is represented as a bar with lateral width indicating the range of estimated f values associated with the amount of gas hydrate formation. The results at the formation temperature of 283.5 K are shown as a bar filled with dots and other results at the formation temperature of 273.5 K. The dotted lines represent the expected isotopic changes during gas hydrate formation with the batch-type isotopic fractionation. Solid curves represent those with the Rayleigh-type isotopic fractionation. The intervals of these variations are 0.0004 for oxygen (a), and 0.004 for hydrogen (b).

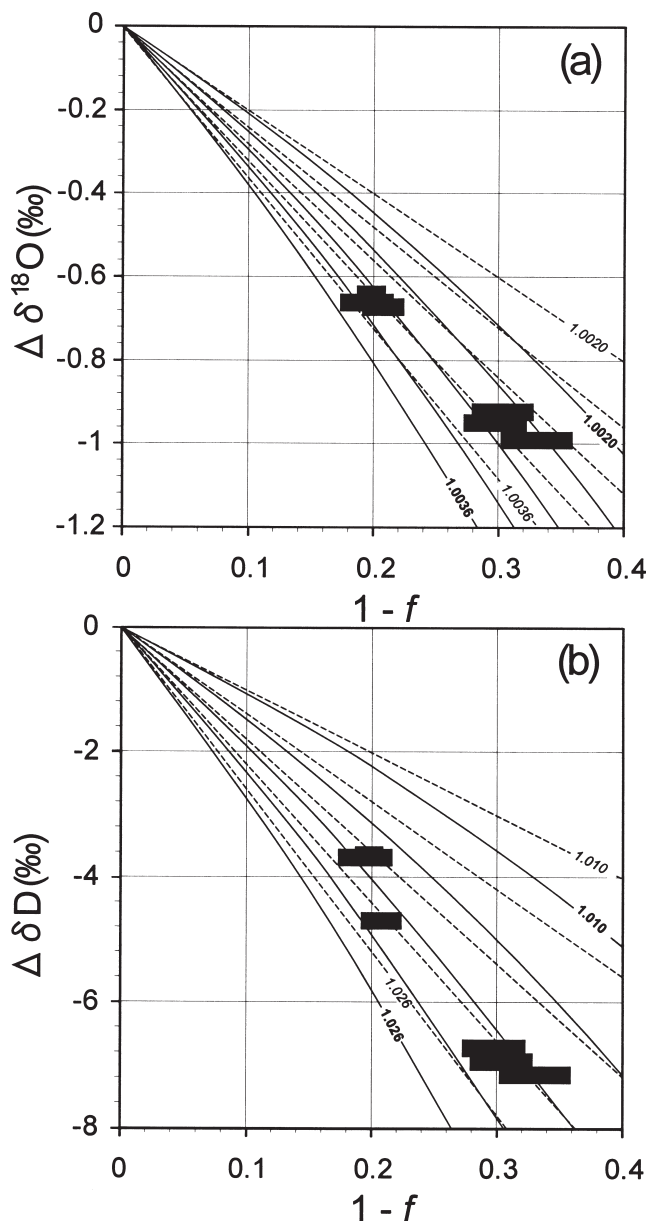


Fig. 3. Results of isotopic fractionation of oxygen (a) and hydrogen (b) in water when Structure I hydrate formed in more than 3 wt% NaCl solutions. The bars and the lines show the same meaning as those in Fig. 2.

1.024, respectively and those between Structure I hydrate and liquid water at the formation temperature of 283.5 K are estimated to be 1.0025–1.0033 and 1.014–1.018, respectively. For Structure II hydrate with krypton, the factors of oxygen and hydrogen at 273.5 K are estimated to be 1.0025–1.0032 and 1.017–1.022, respectively.

From the results, little difference of the oxygen fractionation factors among the hydrate structures is observed. On the other hand, a small difference in the hy-

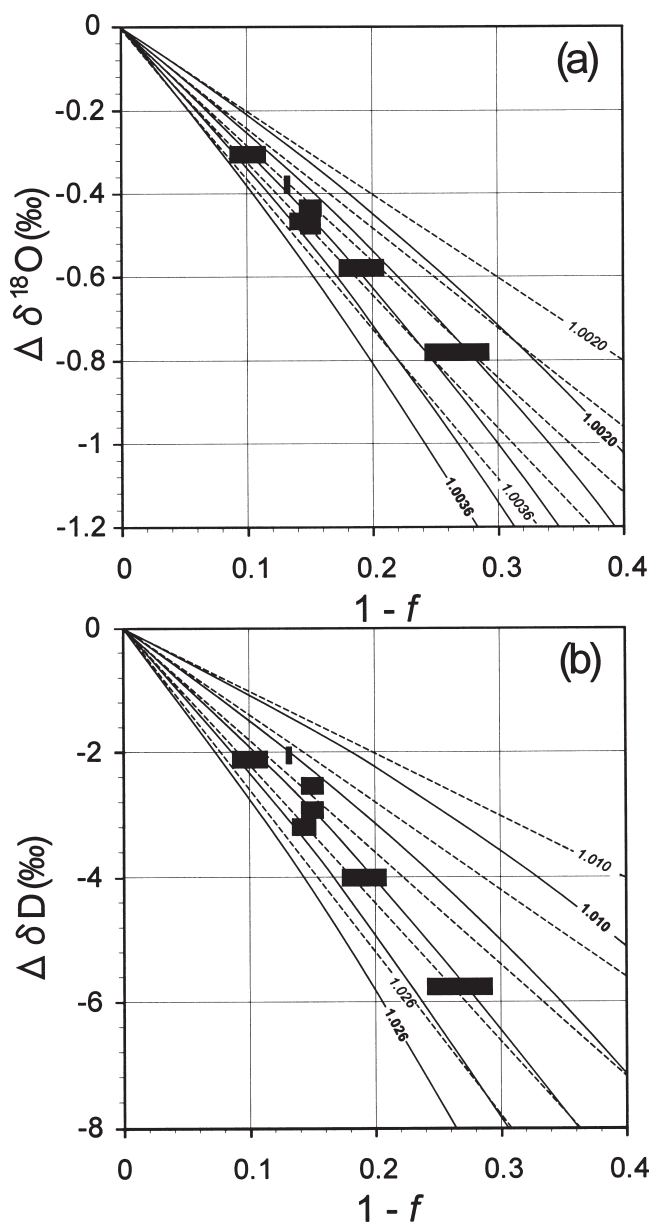


Fig. 4. Results of isotopic fractionation of oxygen (a) and hydrogen (b) in water when Structure II hydrate formed in water. The bars and the lines show the same meaning as those in Fig. 2.

hydrogen fractionation factors among the hydrate structures is observed. The difference of the hydrogen isotopic fractionation factors is estimated to be 0.003. However, considering large analytical errors of isotopic measurements, the compositional changes of hydrogen isotopes during gas hydrate formation observed in this work are comparatively small, resulting in a large uncertainty of determination on isotopic fractionation factors. Therefore, in this work, we cannot recognize the difference of these

hydrate structures beyond the errors of the fractionation factors. Further experiments with smaller analytical errors will be needed to evaluate the difference on gas hydrate structures.

There are little differences in the formation temperatures for Structure I hydrate, however, we have few results to discuss the difference in this work.

For the difference in salt concentration, the factor of hydrogen isotope for saline solutions containing more than 3 wt% NaCl is suggested to be slightly larger than that for liquid water, resulting from the effect of dissolved ions on the isotopic activity in solution (Craig and Hom, 1968). The dissolved salts alter the activities of the isotopic molecules in the solution because of hydration of the ions. Consequently, the isotopic fractionation between gas hydrate and saline solution differs from the fractionation between gas hydrate and pure water. According to Horita *et al.* (1993), the dissolved NaCl has no effect on the fractionation factor of oxygen isotope regardless of salt concentration, while the fractionation factor of hydrogen isotope with 3 to 4.5 wt% NaCl solutions used in this work is estimated to be about 0.002 larger than those with the pure water. The difference of the fractionation factors of hydrogen isotopes obtained by the experiments between liquid water and the saline solution of NaCl is 0.003 to 0.005 which is slightly larger than the estimated values. However, considering large analytical errors and uncertainty of the fractionation process during gas hydrate formation, the difference between experimental and estimated values is not clear. Therefore, the difference of fractionation factors between liquid water and saline solutions of NaCl can be primarily explained by the effect of the dissolved NaCl salt on the activities of isotopic molecules of water because of hydration of its ions.

DISCUSSION

In this work, when gas hydrate forms from liquid water at 273.5 K, the isotopic fractionation factors of oxygen and hydrogen are estimated to be 1.0023–1.0032 and 1.014–1.022, respectively. These values estimated in this work are compared with previous experimental results. Davidson *et al.* (1983) first presented the fractionation factor of oxygen isotope in water between clathrate hydrate and water. They determined the factor of 1.00268 obtained by laboratory experiments on the slow formation of Structure II hydrate of tetrahydrofuran from their solution. Matsumoto and Borowski (2000) estimated the fractionation factor by measurements of oxygen isotope compositions of natural gas hydrates and pore waters recovered from the Blake Ridge, western Atlantic, on Ocean Drilling Program Leg164. According to their results, chloride concentrations and oxygen isotopic compositions in

Table 2. Regression results of least-square fitting of isotopic fractionation factors to experimental data classified by type of hydrate structure, salt concentration and formation temperature. N represents the number of the run. The fractionation factors, α_{GasPres} and α_{NaCl} , were estimated from using f_{GasPres} and f_{NaCl} , respectively. Liquid water is regarded as dilute NaCl solution containing less than 0.2 wt% NaCl, and saline NaCl solution is regarded as that containing more than 3 wt% NaCl.

	N		α_{GasPres}	α_{NaCl}
<i>Oxygen isotope fractionation</i>				
Structure I hydrate(Methane)				
liquid water at 273.5 K	7	batch-type:	1.0032	1.0027
		Rayleigh-type:	1.0028	1.0023
saline NaCl sol. at 273.5 K	6	batch-type:	1.0034	1.0029
		Rayleigh-type:	1.0029	1.0024
liquid water at 283.5 K	2	batch-type:	1.0033	1.0030
		Rayleigh-type:	1.0028	1.0025
Structure II hydrate(Krypton)				
liquid water at 273.5 K	7	batch-type:	1.0032	1.0028
		Rayleigh-type:	1.0029	1.0025
<i>Hydrogen isotope fractionation</i>				
Structure I hydrate(Methane)				
liquid water at 273.5 K	7	batch-type:	1.019	1.017
		Rayleigh-type:	1.016	1.014
saline NaCl sol. at 273.5 K	6	batch-type:	1.024	1.020
		Rayleigh-type:	1.020	1.017
liquid water at 283.5 K	2	batch-type:	1.018	1.017
		Rayleigh-type:	1.015	1.014
Structure II hydrate(Krypton)				
liquid water at 273.5 K	7	batch-type:	1.022	1.019
		Rayleigh-type:	1.020	1.017

pore water sampled within sediments bearing gas hydrates were irregular with sharp spikes. These fluctuations were interpreted to represent differing amounts of gas hydrate contained within the sediment samples. They determined the oxygen isotopic fractionation factors between gas hydrates and ambient pore waters as 1.0034 and 1.0037–1.0040 at each drilling site on the Blake Ridge. The fractionation factors obtained in this work are found to be similar to literature values described above and similar to that between ice and water, which is in the range of 1.0027 to 1.0035 (O'Neil, 1968; Suzuoki and Kimura, 1973; Craig and Hom, 1968; Jakli and Staschewski, 1977), as shown in Table 3.

The isotopic fractionation factor of hydrogen in water between gas hydrate and liquid water has never been reported. The isotopic fractionation factor of hydrogen obtained in this work is found to be similar to that between ice and liquid water of 1.017 to 1.021 (O'Neil, 1968; Suzuoki and Kimura, 1973; Craig and Hom, 1968).

For experiments of Structure II hydrate formation, Davidson *et al.* (1983) suggested that the dominant role of the hydrogen bonding of each water molecule to its nearest molecules in their lattice leads to similarities of

hydrates to ice, and that there is not a significant difference between oxygen isotopic enrichment in ice and Structure II hydrate because the hydrogen bond length and tetrahedral O-O-O angles between water molecules in the hydrate resemble those in ice. Moreover they implied the absence of a significant difference between the oxygen enrichment in Structure I hydrate and ice because the hydrogen bond length and the tetrahedral angles in Structure I hydrate are also similar to those in ice. The results in this work agree with their suggestion of isotopic fractionation in water.

CONCLUSIONS

Isotope fractionation of oxygen and hydrogen in water between gas hydrate and NaCl solution was experimentally investigated in this work. Structure I and Structure II hydrates were formed with methane and krypton gases, respectively. The changes in NaCl concentration and isotopic compositions of water in solution were observed after gas hydrate formation. Little difference of oxygen fractionation factors among the structures of Structure I and Structure II hydrates is observed. On the

Table 3. Comparison of isotopic fractionation factors of oxygen and hydrogen in water between gas hydrate and liquid solution with those between ice and liquid water

Oxygen isotope fractionation		
$\alpha(^{18}\text{O})$		References
hydrate - water		
1.0023–1.0032	Structure I, liquid water	this work
1.0024–1.0034	Structure I, saline NaCl sol.	
1.0025–1.0032	Structure II, liquid water	
1.00268	Structure II, THF sol.	Davidson <i>et al.</i> (1983)
1.0034; 1.0037–1.0040	Structure I, natural pore water	Matsumoto and Borowski (2000)
ice - water		
1.0029; 1.0031		O'Neil (1968)
1.0028		Suzuoki and Kimura (1973)
1.0035 \pm 0.0003		Jakli and Staschewski (1977)
1.00265	dilute NaCl sol.	Craig and Hom (1968)
1.00270	sea water	
Hydrogen isotope fractionation		
$\alpha(\text{D})$		References
hydrate - water		
1.014–1.019	Structure I, liquid water	this work
1.017–1.024	Structure I, saline NaCl sol.	
1.017–1.022	Structure II, liquid water	
ice - water		
1.0178; 1.0195		O'Neil (1968)
1.0206		Suzuoki and Kimura (1973)
1.0195	dilute NaCl sol.	Craig and Hom (1968)
1.0203	sea water	

other hand, a small difference between hydrogen fractionation factors of the hydrate structures was observed, however it was not clear considering large analytical errors and uncertainty of fractionation process. Therefore, in this work, it is difficult to recognize the difference in the hydrate structures. The isotopic fractionation factors of oxygen and hydrogen in water between gas hydrate and liquid water were estimated to be 1.0023–1.0032 and 1.014–1.022, respectively. These factors are similar to those between ice and liquid water.

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