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Chemical Engineering Science 61 (2006) 2670–2674

Chemical Engineering Science

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Structure and thermal expansion of natural gas clathrate hydrates

S. Takeya[a,*], M. Kida[b], H. Minami[b], H. Sakagami[b], A. Hachikubo[b], N. Takahashi[b], H. Shoji[b,**], V. Soloviev[c], K. Wallmann[d], N. Biebow[e], A. Obzhirov[f], A. Salomatin[f], J. Poort[g]

[a] *National Institute of Advanced Industrial Science and Technology (AIST), Central 5, Higashi 1-1-1, Tsukuba 305-8565, Japan*
[b] *Kitami Institute of Technology, 165 Koen-cho, Kitami 090-8507, Japan*
[c] *All-Russian Research Institute for Geology and Mineral Resources of the Ocean, 1 Angliyskiy Avenue, 190121 Saint-Petersburg, Russia*
[d] *Leibniz-Institute of Marine Science, IFM-GEOMAR, Wischhofstr. 1–3, 24148 Kiel, Germany*
[e] *Alfred-Wegener-Institute for Polar and Marine Research, Am Handelshafen 12, 27570 Bremerhaven, Germany*
[f] *V.I. Il'ichev Pacific Oceanological Institute of the Far Eastern Branch of Russian Academy of Sciences, 43, Baltiyskaya Street, 690041, Vladivostok, Russia*
[g] *Renard Centre of Marine Geology, Ghent University, Krijgslaan 281 S8, 9000 Ghent, Belgium*

Received 30 September 2005; received in revised form 21 November 2005; accepted 22 November 2005

Abstract

We report on the structural properties of natural gas hydrate crystals from the Sea of Okhotsk. Using powder X-ray diffraction (PXRD), it was determined that sediments from four locations contained type I gas hydrate, which encage mostly methane (96–98%) and a small amount of carbon dioxide. For all hydrates, the lattice constant was estimated to be 11.85 Å at 113 K, which approximately equals that of pure methane hydrate. The result is in good agreement with the structure of artificially synthesized methane + carbon dioxide mixed-gas hydrates. These results suggest that the lattice constant of the natural gas hydrate does not change due to a change of CO_2 gas content. In addition, the thermal expansion of the sampled hydrate was measured for the temperature range of 83–173 K, and the resulting density of the hydrate crystal at 273 K was estimated to be $0.92\,g/cm^3$. These results are essential for applying natural gas hydrates as an alternative natural fuel resources.

Keywords: Energy; Gases; Chemical analysis; Clathrate hydrate; Thermal expansion

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1. Introduction

Clathrate hydrates, also called gas hydrates, are ice-like inclusion compounds consisting of a hydrogen-bonded crystal of water molecules with cages that contain a guest molecule (Sloan, 1998). Natural gas hydrates are widespread in permafrost and in sediments of continental margins and are recognized as an alternative natural fuel resource because they contain significant amounts of natural gas. It is well known that most natural gases form one of three types of hydrate crystal structure: (1) type I, which is composed of two 12-hedra (5^{12}) and six 14-hedra ($5^{12}6^2$) with a space group Pm3n (Müller and Stackelberg, 1952); (2) type II, which is composed of 16 12-hedra (5^{12}) and eight 16-hedra ($5^{12}6^4$) with a space group Fd3m (Stackelberg and Müller, 1951); and (3) type H, which is composed of three 12-hedra (5^{12}) of one type, two 12-hedra ($4^3 5^6 6^3$) of another type, and a 20-hedra ($5^{12}6^8$) with a space group P6/mmm (Ripmeester et al., 1987). However, the properties of naturally formed natural gas hydrates are poorly understood due to the difficulty of recovering hydrate samples from natural sediments without their dissociation (Davidson et al., 1986; Gutt et al., 1999; Tulk et al., 1999; Yousuf et al., 2004; Chazallon et al., 2005; Kim et al., 2005).

Recent experimental tests on artificially synthesized clathrate hydrates showed a structural transition from type I to II when formed from certain concentrations of methane (CH_4) and ethane (C_2H_6) even though pure CH_4 and C_2H_6 molecules each form type I (Subramanian et al., 2000; Uchida et al., 2002). Structural transitions of pure CH_4 and carbon dioxide (CO_2) hydrate have also been reported (Staykova et al., 2003;

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*Corresponding author. Tel.: +81 29 861 6006; fax: +81 29 861 4506.

**Also corresponding author. Tel.: +81 157 26 9493; fax: +81 157 26 9534.

E-mail addresses: s.takeya@aist.go.jp (S. Takeya), shojihts@mail.kitami-it.ac.jp (H. Shoji).

0009-2509/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.ces.2005.11.049

Schicks and Ripmeester, 2004). In other studies, lattice expansion of the hydrate was observed in $CH_4 + C_2H_6$ mixed hydrates due to a change of gas content (Takeya et al., 2005) and in air hydrate caused by the difference of gas compositions due to a kinetic effect of the air hydrates (Takeya et al., 2000; Ikeda-Fukazawa et al., 2001). These results suggest that hydrate structure is sensitive to the formation conditions and thus prediction of hydrate properties is difficult.

Knowledge of the structure and thermal expansion properties of mixed-gas hydrates such as natural gas hydrate is important for increasing our understanding of intermolecular interactions between guest–host and guest–guest molecules. For example, an increase in the expansivity is attributed to greater anharmonicity in the crystal (Tse, 1987). Larger thermal expansion of CH_4 hydrate than that for hexagonal ice due to guest–host interactions is reported (Shpakov et al., 1998).

For natural hydrates, the density and thermal properties are also of practical importance for better understanding well-logging data (Collett and Lee, 2000) and macroscopic images from the X-ray computed tomography (CT) method (Uchida et al., 2000; Jin et al., 2004; Sato et al., 2005). In this paper we report on the crystal structure and the thermal expansion of natural gas hydrate from the sediments of the Sea of Okhotsk.

2. Material and methods

Natural gas hydrates were obtained from locations northeast of Sakhalin in the Sea of Okhotsk. One sample was obtained at each of four sites during the CHAOS (*Hydro-Carbon Hydrate Accumulations in the Okhotsk Sea*) Project 2003 (Shoji et al., 2005). The samples are shown in Fig. 1 and their sampling locations are shown in Table 1. The samples were obtained using gravity coring and the temperatures of the samples were around 275 K during core recovery. Once the gas hydrate-containing samples were on board they were immediately kept at about 100 K in an atmosphere of nitrogen (N_2) gas. For a comparison sample formed under known conditions, pure CH_4 hydrate was synthesized at 9.1 MPa and 275.4 K using a high-pressure vessel of volume $1.5 \times 10^{-4}\,m^3$. The sample was formed by contact reactions between 30-ml of liquid water and CH_4 gas with a stirring rate of 1000 rpm.

For structural analysis, we removed only white sections of the natural samples. Finely powdered hydrate samples were put in a quartz glass capillary cell (Hilgenberg; 2.0 mm, 0.01-mm thick, 10-mm long) for powder X-ray diffraction (PXRD) measurements using the Debye–Scherrer method with focusing optics (50 kV, 200 mA; Rigaku model Rint-2000). This method allowed us to make the PXRD measurements with small samples (~50 mg) and also made it possible to make precise measurements with an internal standard sample in the capillary cell. The PXRD measurements was performed by a 2θ step scan mode with a counting time of 5 s/step and a step width of 0.02° in the 2θ range of 5–100°. For temperature-dependent PXRD measurements, fine-powdered hydrate samples were top-loaded on a specimen holder made of Cu and measurements were done using the parallel beam method (40 kV, 40 mA; Rigaku model Ultima III). The PXRD measurements was performed by a $\theta/2\theta$ step scan mode with a counting time of 3 s/step and a step width of 0.02° in the 2θ range of 6–70°. Both PXRD measurements were done using CuKα radiation ($\lambda = 1.5406$ Å) and the measurements were performed below 173 K to prevent hydrate dissociation. Temperature deviations of the sample during measurements were within 1.0 K. Determination of the unit cell parameter was done by a full-pattern profile fitting method using RIETAN-2000 (Izumi and Ikeda, 2000).

3. Results and discussion

The X-ray diffraction profile at 113 K showed that the crystal structures of all four natural hydrate samples were type I. The profiles are shown in Fig. 2. Some peaks are from hexagonal ice. The ice was from frozen water, which would come from hydrate dissociation during core recovery and interstitial sea water. Because type I hydrate has a cubic lattice, only one unit cell parameter, hereafter referred to as the lattice constant, needs to be determined. As an internal standard, the lattice constant of hexagonal ice was fixed at 4.4793 Å for the *a*-axis and 7.3216 Å for the *c*-axis (Röttger et al., 1994). With this standard, the lattice constant of all hydrate samples was approximately 11.85 Å at 113 K (see Table 1). The fact that a single lattice constant was obtained despite differences in gas content in the four samples suggests the following. (1) Because CO_2 is the second largest gas component in the natural gas hydrates of the Sea of Okhotsk, the results suggest that the lattice constant of the natural gas hydrate is independent of the CO_2 gas content. This result is consistent with a previous study of artificial $CH_4 + CO_2$ mixed gas hydrates (Takeya et al., 2005). (2) The natural hydrates formed in seawater, but impurities from the ocean such as minerals apparently had a negligible influence on their lattice constant due to desalinization effect. (3) The natural hydrates formed under different depth, which corresponds to different pressure condition, and at same temperature, the depth difference apparently had a negligible influence on their lattice constant.

The increase of the lattice constant with increasing temperature for the natural gas hydrate and pure CH_4 hydrate is shown in Fig. 3. The lattice constant $a(T)$ of CH_4 hydrate was fit to the following function of temperature T from 83 to 173 K following the published data from the previous studies on CH_4 hydrate (Shpakov et al., 1998):

$$a(T) = 11.84 + 5.39 \times 10^{-5}T + 1.78 \times 10^{-6}T^2 (\text{Å}). \qquad (1)$$

The correlation for the fit is 0.99. The results in Fig. 3 show that thermal expansion of pure CH_4 hydrate in this study is within 0.04 Å of previous results on CH_4 hydrate, which corresponds to 0.3% of the lattice constant. For these measurements, the deviation in absolute values is within the instrumental resolution. On the other hand, the thermal expansion can be measured precisely, and this quantity shows good agreement between the natural gas hydrate and the pure CH_4 hydrate. Our results also show that the thermal expansion of the natural gas hydrate is slightly larger than that of pure CH_4 hydrate in the higher temperature region, and is similar to that of CO_2 hydrate (Udachin

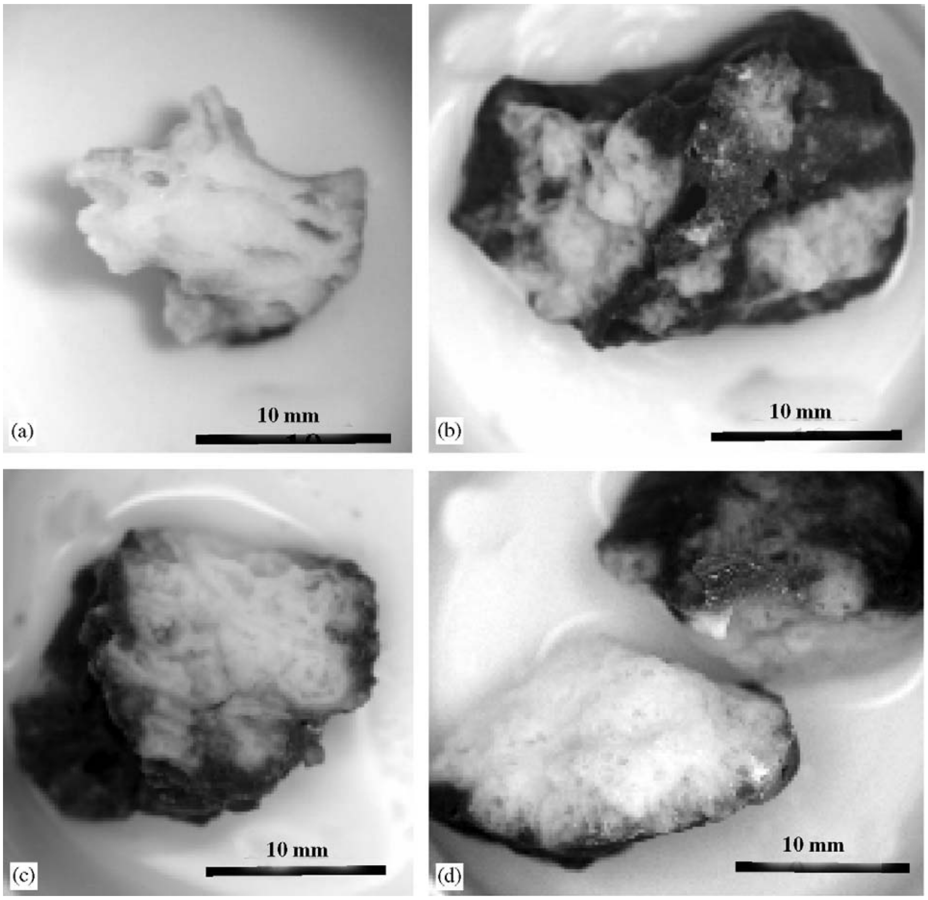

Fig. 1. Hydrate-bearing sediment samples: (a) Kitami 11HC, (b) Kitami 09GC, (c) Hieroglyph 13GC, and (d) CHAOS 16GC.

Table 1
Geological data and measurement results from the natural gas hydrate samples

Sample	Sampling location	Water depth (m) Depth beneath seafloor (m) Temperature at seafloor (K)	Gas content (%)	Lattice constant at 113 K (A)	Cage occupancy $\theta(s)/\theta(l)$ in Udachin et al. (2001)	Density at 113 K (g/cm^3)	Mass ratio hydrate/ice
Kitami 11HC	54°29′59.18″N 144°12′4.56″E	855 0.4 275.5	CH_4: 96.40 CO_2: 3.37 H_2S: 0.23	11.8503(2)	0.91/0.97	0.950	0.449/0.551
Kitami 09GC	54°30′0.29″N 144°12′3.58″E	860 1.1–1.3 275.5	CH_4: 98.21 CO_2: 1.78	11.8516(4)	0.95/0.96	0.950	0.208/0.792
Hieroglyph 13GC	54°30′31.26″N 144°10′43.61″E	830 0–1.7 275.5	CH_4: 98.01 CO_2: 1.98	11.858(4)	0.95/0.96[a]	0.948	0.015/0.985
CHAOS 16GC	54°29′58.27″N 144°17′10.95″E	960 0–4.8 275.5	CH_4: 98.12 CO_2: 1.66 H_2S: 0.21	11.8499(3)	0.89/0.97	0.949	0.319/0.681

The cage occupancies of each hydrate sample were referred the values measured by ^{13}C NMR. [28]

[a] Assumed cage occupancy.

et al., 2001), which is also plotted in Fig. 3. In the case of natural gas hydrate, we obtained the same fit as pure CH_4 hydrate expressed as Eq. (1). The correlation for the fit is 0.97 and the value is slightly lower than that of pure CH_4 hydrate. It suggest that the thermal expansion of the natural gas hydrate almost equaled that of pure CH_4 hydrate, but it might instead suggest that the interaction between the water molecules of the host cages and the CH_4 molecules of the guest molecules changed

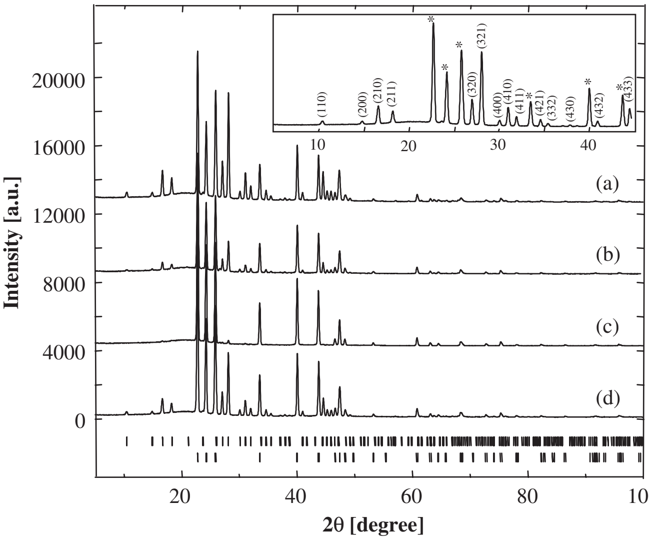

Fig. 2. X-ray diffraction profiles of the samples at 113 K. The upper tick marks are the calculated peak positions for a type I gas hydrate, and the lower tick marks are those for hexagonal ice. The plots are from samples: (a) Kitami 11HC, (b) Kitami 09GC, (c) Hieroglyph 13GC, and (d) CHAOS 16GC. The insert shows the enlarged portion of (a) to designate miller index of each diffraction peak from the hydrate. Asterisks mark the peaks of hexagonal ice in the sample.

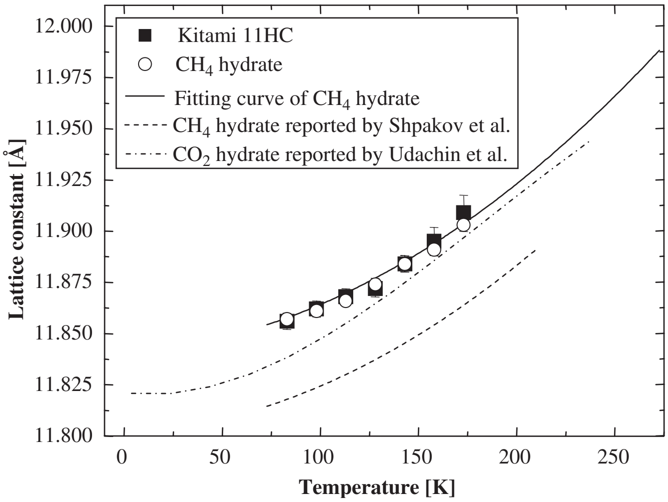

Fig. 3. Lattice constants at a range of temperatures for natural gas hydrate and pure CH_4 hydrate. The solid curve is the fit to the data in this study. For comparison, thermal expansion curves of the lattice constants are shown for pure CH_4 hydrate reported by Shpakov et al. (1998) ($a(T) = 11.80 + 5.39 \times 10^{-5}T + 1.78 \times 10^{-6}T^2$(Å)), and that for pure CO_2 hydrate reported by Udachin et al. (2001) ($a(T) = 11.81945 - 9.08711 \times 10^{-5}T + 4.59676 \times 10^{-6}T^2 - 8.35548 \times 10^{-9}T^3$(Å)).

due to small amounts of encaged CO_2 molecules. However, a higher purity sample or measurements over a wider temperature range is needed to confirm this trend.

To calculate the density of the natural gas hydrate crystals, we assumed that the natural gas hydrates were pure CH_4 hydrate with a cage occupancy that was measured by ^{13}C NMR (Kida et al., 2005). Using the lattice constant estimated from the PXRD analysis, the densities of the natural hydrate crystals are calculated to be 0.95 g/cm^3 at 113 K (see Table 1). Extrapolating the thermal expansivity of the hydrate to 273 K using Eq. (1), the lattice constant is 11.99 Å and the resulting density of the natural gas hydrate crystal would be 0.92 g/cm^3 at 273 K. This value is in good agreement with the value of 0.91 g/cm^3 that was calculated using a thermodynamic model (Sloan, 1998). This suggests that the experimental results are in good agreement with theory. A lattice constant deviation of 0.04 Å corresponds to 0.3% of the lattice constant at 273 K and a deviation in the density of 0.01 g/cm^3.

Finally, the water contents of the samples were estimated using the Rietveld refinement method on the PXRD profile (see Table 1). The resulting mass ratios of the non-sediment parts show that more than 50% of the mass of the white parts of the hydrate samples in Fig. 1 was hexagonal ice, which is frozen water from hydrate dissociation during core recovery and interstitial sea water. Nevertheless, our results show that the remaining natural gas hydrate crystals after core recovery can be used for precise structural analysis.

4. Summary

In this study, the crystal structure and thermal properties of natural gas hydrate from sediments in the Sea of Okhotsk were analyzed using PXRD measurements. We found that the regions containing hydrate composed 2–45% of the mass of the samples, and these regions were type I hydrate with a lattice constant of 11.85 Å and a density of 0.95 g/cm^3 at 113 K. The four samples had differences in CO_2 gas content yet had a lattice constant consistent with a pure CH_4 hydrate. This finding indicated (1) the lattice does not significantly expand or contract with a change of CO_2 gas content and (2) impurities, such as minerals, in the seawater from which the hydrates formed have a negligible influence on the lattice constant due to desalinization effect. (3) The natural hydrates formed under different pressure conditions and at same temperature, the pressure difference apparently had a negligible influence on their lattice constant. The first result agrees with results from experiments on artificial $CH_4 + CO_2$ mixed gas hydrates (Takeya et al., 2005). Also, thermal expansion of the natural gas hydrate in the temperature region from 83 to 173 K was measured, and the result was used to estimate the density of the hydrate at 273 K to be 0.92 g/cm^3. These experimental results show that samples from sediment with only a small amount of hydrate can be used to determine the physical properties of natural hydrate crystals. These chemical analysis carried out in this study will provide the fundamental guidelines for the understanding of natural gas hydrate as an alternative natural fuel resources.

Acknowledgements

This study was supported by grants from Russia (VNIIOkeangeologia, RFBR Grant No. 02-05-64346), from Germany (KOMEX Grant No. 03G0568), and from Belgium (Ghent University Grant FWO-Vlaanderen). S. Takeya thanks

T. Maekawa, H. Fujihisa, Y. Gotoh, and K. Honda, all of AIST, and T. Uchida of Hokkaido University for their valuable comments, and H. Narita of AIST for his help with some of the measurements.

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