Preservation phenomena of methane hydrate in pore spaces

Akihiro Hachikubo,* Satoshi Takeya,* Evgeny Chuvilin and Vladimir Istomin

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Dissociation processes of methane hydrate synthesized with glass beads were investigated using powder X-ray diffraction and calorimetry. Methane hydrate formed with coarse glass beads dissociated quickly at 150–200 K; in this temperature range methane hydrate dissociates at atmospheric pressure. In contrast, methane hydrate formed with glass beads less than a few microns in size showed very high stability up to just below the melting point of ice, even though this temperature is well outside the zone of thermodynamic stability of the hydrate. The rate-determining steps for methane hydrate dissociation within pores are also discussed. The experimental results suggest that methane hydrate existing naturally within the pores of fine particles such as mud at low temperatures would be significantly more stable than expected thermodynamically.

Gas hydrates are guest–host compounds and are crystalline materials consisting of water molecules; these compounds include guest molecules inside hydrogen-bonded water cages. Natural gas hydrates, which contain methane gas as a major component, exist under conditions of low temperature and high partial pressures of the guest gases because they exist in sea/lake bottom sediments and permafrost layers. They are considered to be a possible global source of energy1–3 and are also of concern as a potential source of carbon dioxide4 and a possible global source of energy1–3 and are also of concern as a possible source of global warming by the preservation of methane hydrate5,6 and as a potential source of methane hydrate dissociation.7,8 A comprehensive understanding of the preservation of methane hydrate is important for understanding hydrate-related global climate change.9,10 This preservation phenomenon has been studied, and its mechanism is being identified from a physicochemical point of view.11–16 However, not many studies on gas hydrate stability under natural conditions have been carried out.7,17,18

Powder X-ray diffraction (PXRD) has been widely used to measure dissociation processes of gas hydrates.16,19–21 The PXRD method has advantages for quantitative analysis of the hydrate/ice ratio. We also use calorimetry to measure hydrate dissociation. It is possible to detect heat fluxes resulting from dissociation of hydrate samples by using calorimetry. In this study, the effects of macropores of different sizes (submicron to 100 μm) on the dissociation processes of methane hydrate were examined using PXRD and calorimetry.

Methane hydrate samples formed with glass beads of different sizes were normal structure I (sI) hydrates, as expected. Fig. 1 shows the PXRD profiles for the methane hydrate dissociation process, going from sI to ice, as the temperature increased from 123 to 273 K in steps of 10 K with a 20 scan time of 5 min. Several diffraction peaks assigned to ice become evident at around 163 K, and the peak intensities increase with temperature, whereas the methane hydrate diffraction peak intensities decrease. This indicates that the dissociated methane hydrate was transformed into ice because the equilibrium temperature of methane hydrate at atmospheric pressure is about 193 K. Methane hydrate formed with fine glass beads (COSMO55, see Table S1 (ESI†)) survived up to approximately 250 K, whereas the hydrate formed with coarse glass beads (SPL-100) dissociated at 190 K.

The relative volume ratios for various hydrates were measured by PXRD and were analyzed as a function of temperature (Fig. 2). The hydrate samples coexisting with glass beads larger than 3 μm dissociated quickly, whereas more than 60% of the methane hydrate coexisting with beads smaller...
than 3 μm still remained at 200 K. Dissociation of the hydrate sample stopped at around 190 K, and the secondary stage of dissociation started at 220 K. The dissociation process observed by temperature ramping is the same as the dissociation process for finely powdered pure methane hydrate. The important finding is that the dissociation rates of methane hydrates coexisting with fine glass beads of submicron size were much smaller than that of pure methane hydrate.

The thermographs of the methane hydrate samples are shown in Fig. 3. The primary negative peak, which appeared from 150 K to 200 K, corresponds to the dissociation of methane hydrate. The other peak, which appeared from 265 K to 280 K, arises from ice melting. The thermograph of the hydrate coexisting with glass beads of size 100 μm seemed to be almost the same as that of pure methane hydrate. In contrast, negative peaks of the secondary stage appeared in the temperature region 220–260 K in the case of hydrates coexisting with smaller glass beads. Because these peaks are endothermic and the internal pressures of the cell increased simultaneously over the temperature range, they show that methane hydrate self-preserved within the pores of the glass beads.

In the process of methane hydrate dissociation in a calorimetric system (Fig. S1, ESI†), the inner pressure increased with temperature and reached 0.054–0.060 MPa. The residual ratio of methane hydrate in the sample is estimated from the time variation of the inner pressure (Fig. 4) by assuming that all the surviving methane hydrate was dissociated at 273.2 K. The dissociation curves of methane hydrate coexisting with glass beads larger than several microns show complete dissociation up to 200 K from 150 K. In contrast, in the case of fine glass beads of submicron size, more than 38% of the hydrate still remained at 200 K, although the primary stage (150–200 K) is the same as that for other samples, corresponding to the dissociation temperature of methane hydrate. The secondary stage for the hydrate sample with glass beads of submicron size started from 210 K, and the dissociation progressed slowly up to the melting point of ice. These calorimetric results agree fairly well with the PXRD results (Fig. 2). The difference between the residual ratio obtained by calorimetry and that obtained by PXRD at the same temperature may be the result of differences in the temperature-ramping rate and/or the amount of sample used for each measurement. And the difference might be some inconsistency between the results obtained by these two experimental methods under different atmospheric pressures: calorimetric measurements were started from vacuum condition and the pressure changed as hydrate samples dissociated, while the PXRD was performed under atmospheric pressure of N₂ gas. In any case, these experimental results show that methane hydrates coexisting with glass beads of submicron size are highly stabilized below the melting point of ice.

The effects of the grain size of pure methane hydrate on its dissociation process have already been reported;²¹ the dissociation rate of large hydrate particles was lower than those of smaller particles. It is therefore expected that methane hydrate formed in the small pores of fine glass beads will dissociate easily, according to the grain-size effect. However, this study shows
that methane hydrates within larger pores (several tens of microns to 100 μm) quickly dissociated and that in smaller pores (less than a few microns) they were retained and showed the secondary stage of dissociation.

Fig. 5 shows the apparent specific heat of ice with glass beads plotted against temperature. The apparent specific heat of ice coexisting with fine glass beads (submicron in size) was much larger than that with coarse glass beads (more than 30 μm) above 250 K because of formation of unfrozen water resulting from the capillary effect of macropores.22 The latent heat of fusion of ice was added to the original specific heat of ice and increased the apparent specific heat. The experimental results also suggest the possibility of the existence of unfrozen water even below 200 K. In fact, the existence of a pre-melting ice layer up to 1 nm thick at 193 K in porous silica glass as a result of interaction between water and silica glass has been reported.23 Although we do not have any experimental evidence, the formation of such a water layer on fine silica beads as a result of methane hydrate dissociation could slow down the dissociation rate of methane hydrate in the temperature region above 210 K. Additionally, above 250 K, supercooled water is likely to form as a result of methane hydrate dissociation, as has been reported.24,25 and ice may also be transformed (melt) to unfrozen water as a result of a capillary effect within the fine glass beads. As a result, the amount of water increases in this temperature region and probably plugs pores and reduces methane gas diffusion through fine glass beads; this may reduce the methane hydrate dissociation rate. However, in the case of coarse glass beads, the methane gas leaving the dissociating hydrates is likely to escape easily through the glass beads without such a water layer.

It is well known11 that anomalous preservation of pure methane hydrate occurs above 240 K; this has been confirmed by a rapid-pressure-release method but not by a temperature-ramping method. The experimental results reported in this study confirm anomalous preservation of methane hydrate coexisting with fine glass beads using a temperature-ramping method. Further confirmation of the high stability of methane hydrate coexisting with fine glass beads is expected to be obtained by a pressure-drop method. Thus, further experiments should be performed. Additionally, we need to perform experiments with glass beads in the mesopore range (several nanometres to several tens of nanometres) to further understand methane hydrate dissociation in natural sediments including not only sand but also mud.

**Conclusion**

We studied the dissociation process of methane hydrate formed with different sizes of glass beads. The hydrates within beads of size several tens of microns to 100 μm dissociated quickly. In contrast, methane hydrate formed with fine glass beads showed very high stability up to just below the melting point of ice, even though this is well outside the zone of thermodynamic stability of the hydrate. It is suggested that formation of a water layer on fine silica beads, caused by methane hydrate dissociation, may slow down the dissociation rate of methane hydrate at temperatures above 210 K. The formation of water may induce very high stability of methane hydrate within fine glass beads of submicron size, even in the temperature-ramping method.

**Experimental methods**

Methane hydrate samples were formed from mixtures of water and hydrophilic silica glass beads (see Table S1 and Fig. S2 (ESI†)). About 1 g of fine ice-powder (mean grain size: less than 0.05 mm) and 5 g of glass beads were mixed in a pressure cell (volume: 20 mL) at 255 K. The cell was evacuated and kept at 274.2 K for several hours to melt the ice, and then research-grade methane (99.99% purity, Takachiho Chemical Industry, Tokyo, Japan) was pressurized up to 5 MPa for more than 1.5 d to form methane hydrate. After confirmation of no significant pressure decrease (less than 0.01 MPa h⁻¹), the sample was retrieved from the cell at a temperature below 100 K under a dry nitrogen-gas atmosphere. Mixtures of ice and glass beads without methane hydrate were also prepared by the same method, except for pressurization by methane gas to check the existence of unfrozen water in the sample below the freezing point of ice.

PXRD measurements were performed in a 2θ/θ step scan mode using Cu Kα radiation (λ = 1.541 Å) with a step width of 0.02° in the 2θ range 22-28.52° for a total scan time of 5 min (40 kV, 40 mA; Ultima III, Rigaku, Tokyo, Japan). The hydrate samples formed were ground and then mounted on a PXRD sample holder of depth 0.50 mm, made of Cu, under a nitrogen-gas atmosphere kept below 100 K. Temperature-dependent PXRD measurements from 123 K up to 273 K were performed every 10 K under isothermal temperature conditions. The measurements from 123 K up to 173 K were performed in a vacuum and those from 173 K up to 273 K were performed under a dry nitrogen-gas atmosphere, to prevent vapor condensation on the sample surface, using a low-temperature chamber (Rigaku, Tokyo, Japan). The average temperature-ramping rate was approximately 1 K min⁻¹.

Hydrate-containing samples of about 2.7 g were set into a pressure cell (volume: 3.7 mL) specially designed for a Tian-Calvet-type heat-flow calorimeter (BT2.15, Setaram Instrumentation, Caluire, France), and the dissociation process was monitored. Details of the experimental setup for calorimetry are shown in Fig. S1 (ESI†). A reference cell filled with pure nitrogen was introduced to the calorimeter against room.
temperature fluctuations. The sample cell was set in the calorimeter at 93 K and connected with the other pressure cell (volume: 155.57 mL) for smooth dissociation of the hydrate sample and expansion of the dissociated gas. The total volume of the system was large enough for it to remain under atmospheric pressure, even after hydrate dissociation. The internal pressure of the sample cell was monitored by a pressure gauge (AP-10S, Keyence Corporation, Osaka, Japan) with a resolution of 0.1 kPa. The samples were heated in the calorimeter from 93 K to 298 K at a rate of 0.15 K min⁻¹, and the internal pressure, temperature, and heat flow to/from the sample were recorded. A thermograph from 93 K to 298 K was obtained, and then the sample was dried at 383 K for 24 h. Apparent specific heat measurements of ice with glass beads were also obtained to check the effects of pore size for ice in the same way as for the hydrate samples. The specific heat of ice and latent heat of fusion of ice together constitute the apparent specific heat of ice, obtained by subtracting the thermograph of the dried glass beads from that of the hydrate–glass beads mixture.

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