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Anomalous Preservation of CH₄ Hydrate and its Dependence on the Morphology of Hexagonal Ice

Satoshi Takeya^[a, b] and John A. Ripmeester^{*[a]}

Clathrate hydrates, also called gas hydrates, are crystalline ice-like inclusion compounds consisting of water molecules hydrogen-bonded to form host cages that contain small molecules as guests. Because guest–host interactions play a crucial role, hydrates are thermodynamically stable only when guest molecules occupy the host cages to a certain minimum level. Some gas hydrates can be stored at atmospheric pressure below the melting point of ice (273.2 K) even though this is well outside the zone of thermodynamic stability of the hydrate,^[1] an effect that has been termed self-preservation.^[2] A mechanism for the dissociation of CH₄ hydrate (structure I with space group *Pm3n*) at atmospheric pressure by a temperature-ramping procedure was given in terms of the rate of gas diffusion through an ice layer at temperatures below approximately 200 K.^[3] Above approximately 240 K, delays of CH₄ hydrate dissociation due to ice transformations have been suggested.^[4] However, the existence of unusually enhanced preservation phenomena of CH₄ hydrate as reported by Stern et al. in the temperature region from 240 K to 273.2 K^[5] is one remaining puzzle, a phenomenon which has been termed anomalous preservation. The dissociation rates vary in a reproducible way with two minima at around 250 and 268 K whereas the dissociation is fast below 240 K and appears to be thermally activated. This anomalous preservation has been observed in this temperature region only for CH₄ hydrate upon dissociation by rapid pressure release from the high pressures at which it is stable, to an ambient pressure of CH₄ gas. On the other hand, we recently found that dissociation of gas hydrates by temperature-ramping depends on the interaction strength between guest molecules and H₂O molecules, as reflected by the dissociation pressures of the various hydrates at 273 K.^[6] That work suggests that neither the thermodynamic stability nor the crystal structure, but the nature of the guest molecules determines whether self-preservation phenomena should be expected. Herein, we report the relationship between the morphology of ice grown from hydrate dissociation and hydrate stability in the temperature region of anomalous preservation by the pressure-release method. A comprehensive understanding of the anomalous preservation of gas hydrates is important not

only from a physicochemical point of view, but also for practical applications such as the storage and transport of CH₄ or H₂ gas in the form of solid hydrate^[7] and the understanding of hydrate-related climate change in the earth^[8] and gas reservoirs on the planet.^[9]

The powder X-ray diffraction (PXRD) technique was chosen for this study as it allows us to make in situ measurements under complex sample conditions (*P*, *T*) such as the pressure-release method. Moreover, the method gives quantitative information on crystallographic transformations. Figure 1 shows

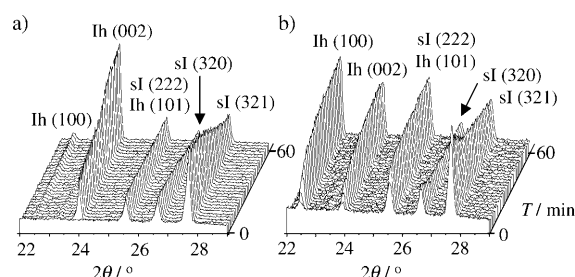


Figure 1. In situ PXRD profiles during the transformation of CH₄ hydrate into ice by the pressure-release method. The initial profile was measured where the hydrate was stable under high pressure. The Miller index of each peak was derived from structure I hydrate (sI) and hexagonal ice (Ih). a) 270.5 K, b) 257.5 K

PXRD profiles of the CH₄ hydrate dissociation process on going from hydrate to ice by rapid pressure release from the high pressure at which the hydrate is stable, to an ambient pressure of the hydrate-forming gas. Each PXRD measurement was done with a total 2 θ -scan time of 2 min with a layer of powdered hydrate 0.3 mm in thickness, which was formed from finely powdered ice in situ in a high-pressure vessel for PXRD measurements.^[10] Only the initial PXRD pattern of each run was done under high pressure, subsequent runs were made under the ambient pressure of the hydrate-forming gas. Isothermal measurements were made at different temperatures: 257.5 K, 268 K, and 270.5 K. Several diffraction peaks assigned to hexagonal ice (Ih) became evident, and these became stronger with time while the hydrate peak intensities decreased. This indicates that the dissociated hydrate transformed into ice Ih. Because the integrated intensity of the X-ray diffraction profile is proportional to the crystal volume, their rates of change are measures of the volume transformation rates.

Figure 2a shows relative volume ratios for CH₄ hydrate in the temperature region from 257.5 to 270.5 K, which was analyzed as a function of time. Here, dissociation rates for the first 20 min. after rapid initial dissociation are estimated to be 9.8×

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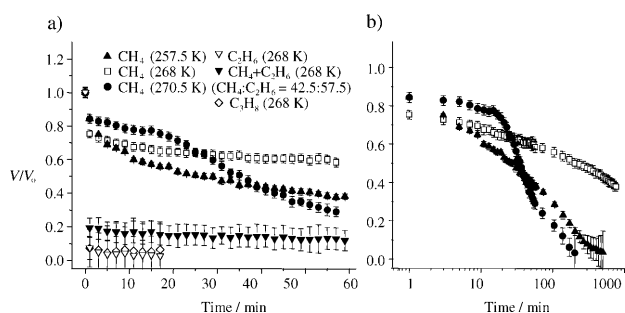


Figure 2. The volume ratio V/V_0 of the dissociating hydrates as a function of time. V_0 is the initial volume of gas hydrate. The relative volume ratios for structure I hydrate were analyzed as a function of time using the peak for the $sl(321)$ crystal plane at around 27.5° in 2θ and those for structure II hydrate were analyzed using peak $sl(511)$ at around 26.5° in 2θ because the integrated intensity of the X-ray diffraction profile is proportional to the crystal volume. a) Linear time scale for initial 60 min, b) Logarithmic time scale showing only CH_4 hydrates.

$10^{-3}\% \text{ s}^{-1}$ at 270.5 K, $8.8 \times 10^{-3}\% \text{ s}^{-1}$ at 268 K, and $2.4 \times 10^{-2}\% \text{ s}^{-1}$ at 257.5 K under an ambient pressure of CH_4 by the pressure-release method. The absolute time values of dissociation for CH_4 hydrate herein are smaller than those reported in the earlier study by Stern et al.,^[5] but the general trend is the same and the difference in absolute values likely are caused by the difference in sample size.^[11] In the case of measurement at 268 K, the CH_4 hydrate was preserved and almost 40% of the hydrate still remained after 12 h even though the stability conditions (2.2 MPa of CH_4 at 268 K) were quite different from those under which the sample was kept. Herein, we illustrate that even a thin layer of CH_4 hydrate 0.3 mm in thickness can show anomalous preservation phenomena. The relative volume ratios during the dissociation of C_2H_6 hydrate, $\text{CH}_4 + \text{C}_2\text{H}_6$ hydrate and C_3H_8 hydrate at 268 K as measured by PXRD were also analyzed. Their dissociation occurred just after the rapid pressure release, even though less than 20% of each hydrate remained after the initial dissociation. The dissociation pressures at 268 K for C_2H_6 hydrate, $\text{CH}_4 + \text{C}_2\text{H}_6$ hydrate (structure I), and C_3H_8 hydrate (structure II with space group $Fd\bar{3}m$) are 0.36 MPa, 0.5 MPa and 0.12 MPa, respectively, and their thermodynamic stabilities are reflected by dissociation pressures that are lower than that of CH_4 hydrate. These hydrates did not show anomalous preservation, this result being consistent with the earlier macroscopic study by Stern et al.^[12] Here, the experimental conditions are almost at the stability condition for C_3H_8 hydrate (268 K, 0.12 MPa of C_3H_8), even though the C_3H_8 hydrate dissociated rapidly. In our previous study, dissociation of C_2H_6 and C_3H_8 hydrate under atmospheric pressure of N_2 gas proceeded in a single step up to 220 K whereas the dissociation rate for CH_4 hydrate decreased and as the sample self-preserved up to 268 K during temperature ramping.^[6] Additionally, it has been reported that $\text{CH}_4 + \text{C}_2\text{H}_6$ hydrate dissociates as a single entity without preferential release of either CH_4 or C_2H_6 .^[13] Therefore, the preservation of gas hydrates by the rapid pressure-release method also depends on the nature of the guest molecules, but not on either the thermodynamic stability or the crystal structure.

The initial dissociation of the CH_4 hydrate is fast and then becomes slower, as shown in Figure 2. This trend is consistent with earlier studies that the initial growth of ice is due to nucleation and lateral growth that covers the hydrate with a coating of ice, and the slower part of the growth occurs after the surface is completely coated with ice.^[3] To clarify the distribution of dissociating hydrate and transformation to ice within a thin layer of the hydrate, grazing incident XRD measurements were done using a CH_4 hydrate sample 1.0 mm in thickness synthesized by the procedure mentioned before. Figure 3

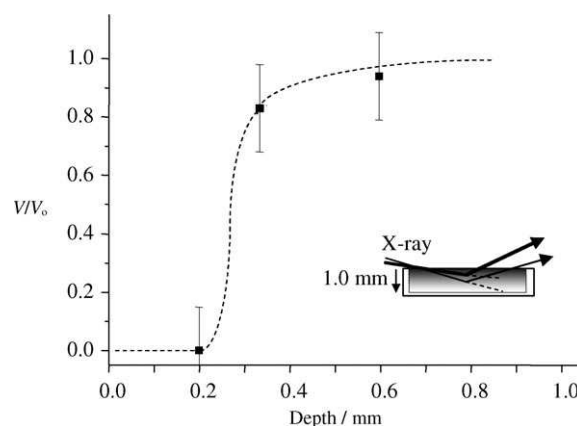


Figure 3. The volume ratio V/V_0 of the dissociating CH_4 hydrate as a function of depth within the hydrate layer after about 40% of the hydrate had dissociated. V_0 is the initial volume of the gas hydrate. Because the ratio of the integrated intensity of the X-ray diffraction profile is proportional to the crystal volume, the relative volume ratios of the hydrate were analyzed for ice Ih transformed from the hydrate using grazing incidence XRD for the $lh(002)$ crystal plane at around 24.0° in 2θ . The inset shows a cross-sectional image of the hydrate and grazing incident XRD. The dotted line is only a guide.

shows relative volume ratios of CH_4 hydrate as a function of depth within the CH_4 hydrate layer, which was measured from the $lh(002)$ diffraction peak after hydrate dissociation of about 40% to complete dissociation at 270.5 K. Here, the values of depth correspond to the penetration depth of $\text{CuK}\alpha$ radiation by assuming ice Ih crystals with a 100% packing ratio. It clearly shows that the ice grown due to hydrate dissociation is concentrated only at the surface of the dissociating thin hydrate layer, even though absolute values of ice thickness may change caused by the difference in sample size and thermal history. This result suggests that the thin layer of CH_4 hydrate began to dissociate from the surface and the thickness of the ice layer increased as hydrate dissociated. Accordingly, it is concluded that the surface coating of ice Ih controls dissociation of CH_4 hydrate even in the temperature region of anomalous preservation.

Figure 4 shows time-dependent relative intensity ratios of the $lh(002)$ to $lh(100)$ peaks measured by PXRD. For CH_4 hydrate, the relative intensity ratio at 257.5 K was consistent with the theoretical value for ice Ih, $I_{002}/I_{100} \sim 0.5$, but the relative intensities at 268 K and 270.5 K were significantly larger. It is known that the morphology of ice Ih grown in a vapor phase of air switches from plate-like crystals (~ 271 K), which has ex-

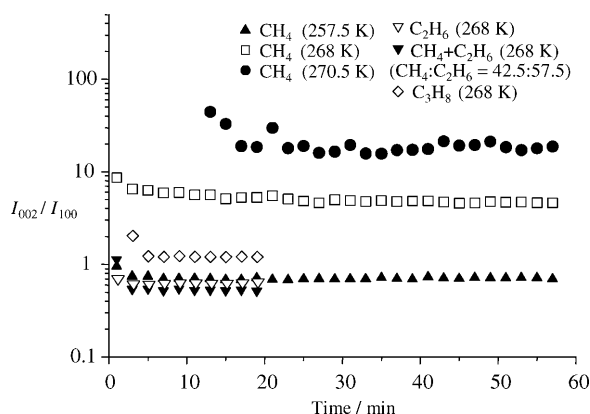


Figure 4. Time dependence of the intensity ratio of the $lh(002)$ to $lh(100)$ peaks during the transformation from gas hydrates to ice. Here, initial values for the CH_4 hydrate at 270.5 K are not shown because the I_{002}/I_{100} ratios are at infinity: intensities of (100) are almost zero whereas those of (002) are strong enough, as shown in Figure 1a.

tended (001) crystal planes, to columns (~ 268 K), to plates (~ 258 K), and to predominantly columns (< 243 K) as the temperature decreases.^[14] Because the flow of heat, the plate-like ice likely grows in a horizontal orientation in the sample holder as the growth of ice Ih is due to the exothermic reaction. Here, it should be noted that the formation of plate-like ice was not induced by preferential orientation of the CH_4 hydrate crystals because the hydrate PXRD patterns before dissociation were consistent with the ideal values for the random orientation of crystals, as reported earlier.^[15] Therefore, the experimental results for CH_4 hydrate herein suggests the formation of plate-like ice Ih crystals on the surface of the hydrate layer at 268 K and 270.5 K, while the formation of randomly oriented smaller-sized ice Ih crystals occurs at 257.5 K. This is supported by earlier cryo-scanning electron microscope (cryo-SEM) observations^[12, 16] that anomalously preserved hydrate is a uniformly dense material while as-synthesized hydrate has a macroscopically granular appearance.

In the case of C_2H_6 , $CH_4 + C_2H_6$ and C_3H_8 hydrates at 268 K, the changes in the PXRD profile with time suggested that neither anomalous preservation nor growth of plate-like ice Ih crystals took place. Here, the initial dissociation rates may depend on the type of guest molecules; C_2H_6 and C_3H_8 hydrates dissociate readily but CH_4 hydrate is self-preserved during temperature ramping as reported earlier.^[6] It is also reported that morphologies of ice change depending on the type of atmospheric gas present during growth, for example, air, N_2 , O_2 , CO_2 and H_2 , even though the mechanism is poorly understood.^[17] The difference in ice morphology depending on guest molecules may change the dissociation rates of gas hydrates. Subsequently, the rapid dissociation of the hydrates will also give higher levels of water saturation, and this may well lead to more complex morphologies for the ice that is formed, dendrites or needles instead of plates or columns under the isothermal condition used.^[14] The former morphologies are much more likely to produce a porous ice layer than extended plates, thus further hydrate dissociation should occur readily. In fact, recent in situ direct observations by using a scanning

confocal microscopy show formation of a transparent ice sheet on dissociating CH_4 hydrate while small ice particles form on dissociating C_2H_6 hydrate by the pressure-release method.^[18] Accordingly, it is concluded that the formation of the plate-like ice Ih crystal leads to the onset of anomalous preservation induced by the rapid pressure-release method. We suggest that plate-like ice Ih crystals are more likely to inhibit the dissociation of CH_4 hydrate than aggregated ice crystals of other morphologies or different crystalline phases of ice, formed by temperature ramping above 240 K.^[4] In turn, anomalous preservation is shown to depend on the morphology of the ice Ih grown, which depends strongly on the thermal history of the hydrate samples as well as the nature of the guest molecules.

The dissociation ratio of CH_4 hydrate at 270.5 K shown in Figure 2b was the smallest for the initial 20 min for the three experimental runs. Over the initial period of about 20 min, it is suggested that the dissociating CH_4 hydrate was almost completely covered by ice crystals with horizontally oriented $lh(001)$ planes from the I_{002}/I_{100} ratio (Figure 4). However, the dissociation rate at 270.5 K increased subsequently with decreasing I_{002}/I_{100} ratios. The change in slope of the dissociation rate with time suggests a change in one of the physical properties of ice Ih close to its melting point. Formation of a supercooled liquid-like phase and changes in its thickness or transformation into ice would be one such possibility, as suggested by visual observations and thermodynamic calculations.^[19] It has been reported that such crystals with horizontally oriented $lh(001)$ planes grow at the surface of supercooled liquid water at temperatures just below the melting point of ice Ih,^[20] thus the existence of such a layer also supports the growth of plate-like ice crystals. At the same time, a mobile water layer may help anomalous preservation in a number of ways for example, it may support the contact between the dissociating hydrate and ice that forms, or it may seal the plate-like crystals together to give a tight envelope around the dissociating hydrate. In the case of the diffusion-limited hydrate dissociation model,^[3, 4] it is applicable only in case when the hydrate-forming gas phase (such as that in voids whose internal pressure corresponds to the dissociation pressure of gas hydrate) exists between the ice layer and the hydrate. It suggests that the ice layer needs to be strong enough to withstand the large pressure difference between the dissociation pressure and atmospheric pressure—such as the pressure difference of 2.3 MPa at 270.5 K for CH_4 hydrate—while the fracture strength of granular polycrystalline ice decreases with increasing temperature and increasing grain size of ice.^[21] Nevertheless, the thickness of the ice layer covering the dissociating CH_4 hydrate at 270.5 K is estimated to be less than 0.1 mm according to the volume ratio of the preserved CH_4 hydrates in Figure 2. On the other hand, it is known that single crystals of natural air ($N_2 + O_2$) hydrate tightly enveloped in an ice crystal, as recovered from the ice sheet in polar regions, are preserved under atmospheric pressure for several years. It is reported that the onset of dissociation of the natural air hydrate occurs only after the nucleation of air bubbles at the boundary of air hydrate and the surrounding ice at 263 K.^[22] This is yet more evidence for the high stability of tightly enveloped gas hydrate just below

the melting point of ice, even though the mechanical strength of a thin ice layer is not strong.

Herein, the occurrence of anomalous preservation of CH₄ hydrate was observed in the temperature region from 257.5 K to 270.5 K using the in situ PXRD technique during dissociation by rapid pressure release. The distinct morphologies of ice Ih that appear when hydrate dissociates under different temperature–pressure profiles were correlated with the occurrence of anomalous preservation: plate-like ice crystals grew upon dissociation by rapid pressure-release, and aggregated ice crystals transformed by sintering finely powdered ice crystals grew upon dissociation by temperature-ramping. The formation of the plate-like ice crystal accompanies the onset of the anomalous preservation of gas hydrates. Then, a mobile water layer may also support the contact between the dissociating hydrate and the plate-like ice Ih. Additionally, it was suggested that the nature of the ice crystals and the interaction between guest molecules and H₂O molecules^[6] both affect anomalous preservation phenomena for gas hydrates. We think that the gas hydrates which show self-preservation phenomena by the temperature-ramping method in earlier studies,^[6,23] such as N₂, O₂, Ar, and H₂ hydrate, will also show anomalous preservation by the rapid pressure-release method. Preservation phenomena for hydrates of these binary gas systems are also expected. In addition, anomalous preservation phenomena for the CH₄ + C₂H₆ mixed gas hydrate upon dissociation by the rapid pressure-release method is also expected, depending on the exact gas composition.

Experimental Section

Gas hydrate samples were synthesized from fine ice Ih powder in a high-pressure vessel specially designed for PXRD.^[10] Finely powdered ice samples were mounted on a PXRD sample holder made from Cu under a N₂ gas atmosphere kept below 100 K: the thickness of the ice powder layer was 0.30 mm to avoid temperature gradients within the sample. The sample holder with the ice powder was then loaded into the high-pressure vessel kept below 263 K. Then, hydrate-forming gas, CH₄, C₂H₆, CH₄ + C₂H₆ (CH₄:C₂H₆ = 42.5:57.5) and C₃H₈ was supplied slowly from high-pressure cylinders until the pressure inside the vessel was increased up to 5.0 MPa for CH₄, 1.0 MPa for C₂H₆, 2.2 MPa for CH₄ + C₂H₆ and 0.5 MPa for C₃H₈, respectively. The temperatures of the sample were slowly raised up to 274 K to transform all ice into gas hydrate. Then the temperatures of the sample were set to the temperatures for the decomposition run. After confirming that almost all of the ice sample transformed into hydrate by PXRD, dissociation measurements of each gas hydrates by the rapid pressure-release method were performed at a constant temperature with a maximum deviation of 0.5 K and the pressure was left to be ambient under the hydrate-forming gas. In situ PXRD measurements were done in θ/θ step scan mode using CuK α radiation (λ = 1.542 Å) with a step width of 0.04° in the 2 θ range of 22–29° every 2.0 min (40 kV, 40 mA; BRUKER axs model D8 Advance equipped with solid-state detector model LynxEye). Grazing incident XRD measurements were done using the same diffractometer in detector fix mode. The angle of the incident X-ray tube with 0.10 mm divergence slit was fixed at 3.0, 5.0 and 9.0 degree to measure diffraction from different depths within a hydrate layer of 1.0 mm in thickness.

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