

Observation of Clathrate Hydrate Grown in Interparticle Spaces

The phase-contrast X-ray imaging technique with synchrotron X-ray radiation is a unique way of identifying gas hydrates coexisting with ice and water. In this study, we successfully observed THF hydrate grown in interparticle spaces at temperatures below and above ice point (273 K). This nondestructive imaging method without any contrast dye can be used to observe natural gas hydrates formed under natural settings.

Clathrate hydrate (so-called gas hydrate) is an ice-like crystal which is a host-guest inclusion compound containing water molecules as host. Natural gas hydrate, which contains natural gas as guest, exists at the bottom of the ocean or in permafrost layers, and is considered to be an unconventional natural gas resource. To predict the occurrence of natural gas hydrate in the natural setting, nondestructive observation of gas hydrate in sediments is a valid and feasible approach. X-ray absorption coefficients for the hydrates are almost the same as those of ice and water, and so natural gas hydrates coexisting with ice (or water) have not been distinguished using conventional non-destructive imaging techniques. Thus, earlier studies focused on the distribution of icy materials (mixture of gas hydrate and ice) in sediments. The magnetic resonance imaging (MRI) technique allows identification of gas hydrates coexisting with liquid water, but it has not been used for a system coexisting with ice. In contrast, the phase contrast X-ray imaging technique is unique in that it can identify gas hydrates coexisting with both liquid water and ice [1, 2]. In this study, we performed in-situ observation of tetrahydrofuran (THF) hydrate growth as a substitute for natural gas hydrate in interparticle pore space using a phase contrast X-ray imaging method by means of X-ray interferometer imaging (XII) with a spatial resolution of about 40 μm [3].

For the experiments, THF solution of about 19 wt%, which corresponds to the stoichiometric ratio of THF (1 mol) to H_2O (17 mol), was introduced into a cylindrical-shaped sample cell (ϕ 12 mm) made from polypropylene filled with polyethylene (density: $\sim 0.95 \text{ g/cm}^3$) beads of 3.2 mm in diameter (see Fig. 1a). The sample cell was mounted into a cryo-chamber equipped with an X-

ray imaging system, and then THF hydrate was formed in the cryo-chamber at 253 K. Phase contrast X-ray imaging was performed at a vertical wiggler beamline (BL-14C) at the Photon Factory using 35-keV monochromatic synchrotron X-rays. To obtain a phase contrast X-ray CT image, gas hydrate samples were rotated 180° in 0.72° steps. More experimental details are reported elsewhere [3].

Figure 1b shows a three-dimensional (3D) XII image of Fig. 1a, after processing to clarify the THF

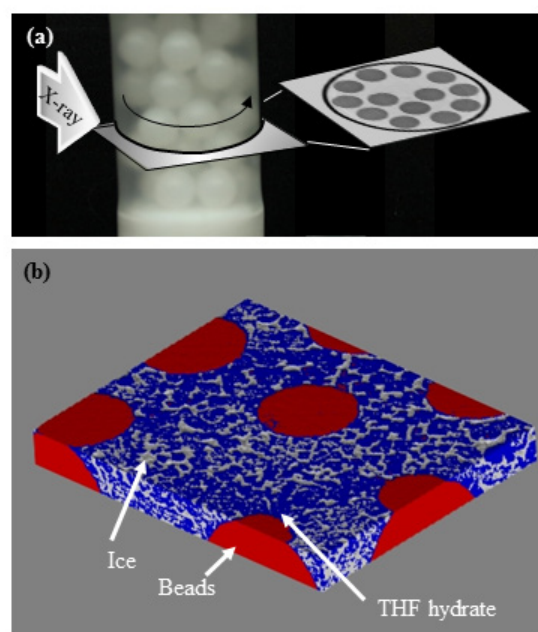


Figure 1: (a) Cylindrical-shaped sample cell containing polyethylene beads and its cross section image, (b) Phase contrast X-ray CT image of THF hydrate grown in interparticle pore at 253 K.

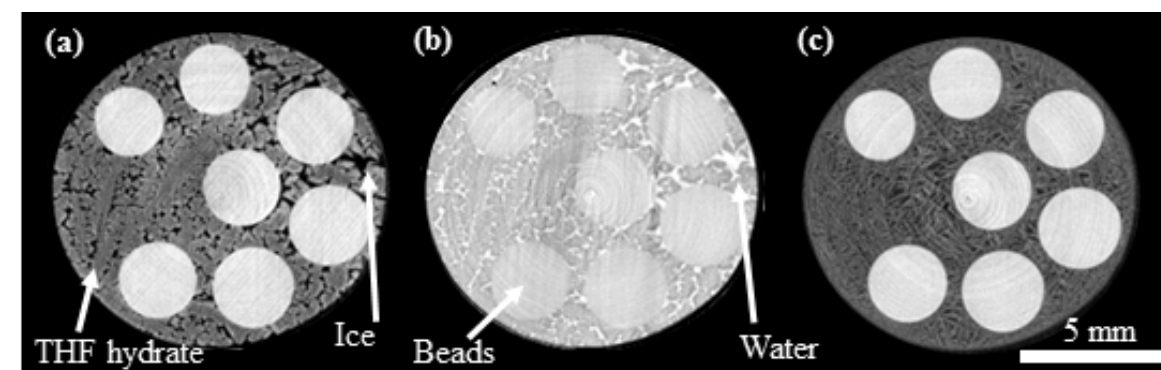


Figure 2: THF hydrate grown in interparticle pore measured at (a) 253 K. The temperature of the sample was increased to (b) 276 K to melt the ice coexisting with THF hydrate. Then it was heated to 283 K for the dissociation of THF hydrate, and was cooled to (c) 253 K for the re-growth of THF hydrate.

hydrate grown. The image shows that the ice region, where THF hydrate did not grow, is randomly distributed. Figure 2 shows the cross section of the cylindrical-shaped sample cell at different temperatures. Here, circles correspond to the cross section of the beads. The black spotty areas correspond to the area with the smallest density, which corresponds to ice (density: 0.92 g/cm^3). In contrast, the white spotty areas correspond to the area with the largest density, which corresponds to liquid water (density: 1.00 g/cm^3). Accordingly, the intermediate gray-colored areas correspond to THF hydrate (density: 0.97 g/cm^3). Comparing Fig. 2a measured at 253 K and Fig. 2b measured at 276 K, it is clear that the ice area melted and changed into water without any change in texture of THF hydrate. After the measurement of Fig. 2b, the temperature of the sample was increased up to 283 K for the dissociation of THF hydrate. Then, it was cooled to 253 K for the re-growth of THF hydrate. As a result, needle-like THF hydrate crystals grew as shown in Fig. 2c.

In this study, we used polyethylene beads, but not silica ($\sim 2.2 \text{ g/cm}^3$) beads, for the XII imaging. As a result, we succeeded in visualizing THF coexisting with ice and water in interparticle space. So far, we have succeeded in visualizing CH_4 hydrate or natural gas hydrate coexisting with ice even though the density

differences are less than 0.01 g/cm^3 . Therefore, the experimental method reported here can be applied to the CH_4 hydrate system. To the best of our knowledge, this is the first visualization of gas hydrates from a temperature below and above 273 K with the same experimental method. Accordingly, the method using XII imaging reported in this study paves the way for visualizing the distribution of gas hydrates, which is important for understanding the physical properties of natural gas hydrate sediments.

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BEAMLINE

BL-14C

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