CAN HYDRATE DISSOLUTION EXPERIMENTS PREDICT THE FATE OF A NATURAL HYDRATE SYSTEM?

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Here, we present a dissolution study of exposed hydrate from outcrops at Barkley Canyon. Previously, a field experiment on synthetic methane hydrate samples showed that mass transfer controlled dissolution in undersaturated seawater. However, seafloor hydrate outcrops have been shown to have significant longevity compared to expected dissolution rates based upon convective boundary layer diffusion calculations. To help resolve this apparent disconnect between the dissolution rates of synthetic and natural hydrate, an in situ dissolution experiment was performed on two distinct natural hydrate fabrics.

A hydrate mound at Barkley Canyon was observed to contain a “yellow” hydrate fabric overlying a “white” hydrate fabric. The yellow hydrate fabric was associated with a light condensate phase and was hard to core. The white hydrate fabric was more porous and relatively easier to core. Cores from both fabrics were inserted to a mesh chamber within a few meters of the hydrate mound. Time-lapse photography monitored the dissolution of the hydrate cores over a two day period. The diameter shrinkage rate for the yellow hydrate was 45.5 nm/s corresponding to a retreat rate of 0.7 m/yr for an exposed surface. The white hydrate dissolved faster at 67.7 nm/s yielding a retreat rate of 1.1 m/yr. It is possible these hydrate mounds were exposed due to the fishing trawler incident in 2001. If these dissolution experiments give a correct simulation, then the exposed faces should have retreated ~ 3.5 m and 5.5 m, respectively, from 2001 to this expedition in August 2006. While the appearance of the hydrate mounds appeared quite similar to photographs taken in 2002, these dissolution experiments show natural hydrate dissolves rapidly in ambient seawater. The natural hydrate dissolution rate is on the same order as the synthetic dissolution experiment strongly implying another control for the dissolution rates of natural hydrate outcrops. Several factors could contribute to the apparent longevity of these exposed mounds from upward flux of methane-rich fluid to protective bacterial coatings.

Keywords: marine hydrate, climate, carbon cycle
INTRODUCTION
Gas hydrates are naturally occurring compounds found in the World’s permafrost and oceans [1]. Current research interests in natural hydrates include their possible use as a future energy resource and implications for climate change and seafloor stability. In the natural environment, sufficient temperature and pressure conditions for hydrate formation exist over a vast portion of the ocean. However, in addition to pressure and temperature, the chemical potential of the gas in the hydrate must be equal to the surrounding waters. If the concentration of the gas in surrounding water is under-saturated with respect to the gas in the hydrate, the hydrate will dissolve to drive the system towards chemical equilibrium [2].

Natural hydrate deposits typically exist in sediments below the sulfate reduction zone and can persist to the base of the hydrate stability zone [3]. These hydrates are thought to be insulated from small variations in pressure and temperature. However, there are other oceanic hydrates which exist very close to the seafloor in areas of high fluid or gas flux [4]. In some cases, hydrate mounds are found exposed on the seafloor [5, 6]. Thermodynamically, gas hydrates, such as seafloor hydrate mounds exposed to ambient seawater, are expected to be in under-saturated conditions and dissolve over time.

To date, little work has been done on the rate at which this dissolution occurs. The majority of hydrate dissociation work has focused on heat-transfer controlled systems, more relevant to oil and gas pipeline blockages [7]. The only field study that has been performed was on laboratory synthesized CH₄ and CO₂ hydrates exposed to ambient under-saturated seawater around 1000 meters depth in the Monterey Bay [2]. These experiments showed that mass transfer was controlling the dissolution process. However, the experimental rate of dissolution for these synthetic samples appears to be too rapid compared with some in situ observations of hydrate mounds. For example, little visual change was observed over a 350 day period for a hydrate mound at Bush Hill, Gulf of Mexico [8]. In the case of Bush Hill, sII hydrates were formed in close contact with a light condensate/oil phase. The open question remains to why the morphologies of these hydrate mounds can show only small changes over time. In order to understand this situation better, field work was performed at Barkley Canyon.

Barkley Canyon (Figure 1) is located off Vancouver Island on the northern Cascadia Margin accretionary prism. Originally discovered by a fishing trawler, hydrate exists as mounds on the seafloor [9]. At around 850 m depth, the hydrate field is estimated at 0.5 km² with hydrate both exposed and veiled with a thin layer of sediment, on the order of centimeters in thickness [5]. A light yellow condensate fluid is present in the surrounding sediment and associated with the hydrate, causing yellow staining [10]. With the buoyant hydrate slabs on the seafloor reaching 7 m in length and 3 m in height and with only a thin sediment cover, the hydrate mass must continue deeper and be anchored below the surface. Previous studies at the site have shown the hydrate to have thermogenic origins, with both sII and sH hydrate structures present [10].

Figure 1 Map of Barkley Canyon located off Vancouver Island. Water depth from a MBARI AUV mapping survey in August 2006 [11].

METHODS
All field measurements were carried out during a survey of Barkley Canyon conducted on August 9-17, 2006, aboard the MBARI R/V Western Flyer using the remotely operated vehicle (ROV) Tiburon. Exposed outcrops of gas hydrates were cored using a specially constructed stainless steel coring device, with an internal volume of 88 cm³. The leading edge of the corer had a serrated rim.
Inside the corer was a hydraulic ram to eject the hydrate core. Hydrate samples were cored directly using the ROV manipulator arm and then injected into a sampling cell. For the hydrate dissolution experiment, the hydrate was added to an open mesh exposure container, which allowed for exposure to ambient benthic currents with minimal disturbance.

In order to observe the slow dissolution of the hydrate in seawater at Barkley Canyon, we elected to use time-lapse photography. The hydrates were measured for a total time of around 54 hours. This technique was similar to the approach for measuring the slow dissolution of synthetic hydrate specimens in Monterey Bay [2]. The time-lapse photography was performed using a Nikon Cool-pix 3 megapixel camera set to record an image at 10 minute intervals. The camera, along with lighting and a battery pack, was mounted on a custom benthic elevator. The open mesh exposure chamber was positioned on the elevator at a pre-determined distance for optimal illumination and resolution. In addition to the time-lapse photographs, frame grabs from the high definition (HD) video recorded on multiple visits by the ROV were also analyzed. The elevator was located in close proximity to the hydrate mounds (< 25 m) with the exposure chamber located near the seafloor (<2 m). The ambient conditions were 4.17 °C, 868 dbar hydrostatic pressure (8.78 MPa total pressure), and S=34.23-34.25.

Changes in the hydrate core over the dissolution process were determined in post-cruise analysis of the time-lapse photographs and HD frame grabs. Two independent analyses were performed using Photoshop® and ImageJ [12] to estimate the hydrate core’s dimensions as a function of pixel number. The pixel length scale was calibrated in each photograph based on a known dimension of the open mesh container. Each length and diameter of a hydrate core was taken as an average of three measurements across the core.

Molar gas flux based on measured dissolution rate is calculated by

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DR = \frac{SR}{2} \cdot \frac{\rho_{\text{hydr}}}{M_{W_G}} \cdot \frac{M_{W_G}}{M_{W_G} + 0.018 n}
\]

where \( DR \) is the dissolution rate in mmol gas/(m\(^2\) s), \( SR \) is the measured shrinking rate of the cores in mm/s, \( \rho_{\text{hydr}} \) is the hydrate density (938 kg/m\(^3\) for the yellow hydrate fabric, 925 kg/m\(^3\) for the white hydrate fabric), \( M_{W_G} \) is the average molecular weight of the gas in the hydrate (21.4 g/mol for the yellow hydrate and 18.6 g/mol for the white hydrate), and \( n \) is the overall hydration number (6.4 for the yellow hydrate and 6.3 for the white hydrate). The density, average molecular weight, and overall hydration number were all calculated based on the measured hydrate composition [13].

RESULTS AND DISCUSSION

One of the hydrate mounds, dubbed “double mound”, was of particular interest. Two distinct hydrate fabrics were present in the hydrate mound as shown in Figure 2: a “yellow” hydrate, stained with a light condensate, and a “white” hydrate, which was not associated with the condensate phase. Comparing the two hydrate fabrics, the yellow hydrate was much more resistant to coring. When a fractured sample of a yellow hydrate core was placed in a glass cell, the condensate was observed to float to the top of the cell; this separation of the condensate and hydrate revealed a white/clear hydrate. This indicated that the condensate was trapped in veins throughout the hydrate mounds, not as bubbles or pockets in the bulk hydrate. The white hydrate was cored relatively quickly and small gas bubbles were observed escaping during the coring.

![Figure 2 The “double mound” site at Barkley Canyon. This mound had two distinct hydrate fabrics present: a yellow oil-stained fabric overlaying a white more-porous fabric.](image-url)
Hydrate fabric porosities

For hydrate dissolution in under-saturated seawater, a major component of the diffusional driving force is the hydrate composition. In order to determine the gas compositions of the two fabrics, a gas funnel containing a 240VDC 400 W heating element was used. A hydrate core was injecting into the inverted heated funnel shown in Figure 3. The heater then caused hydrate to dissociate allowing the gas to collect in the top of the funnel. The gas was collected inside 150 ml evacuated stainless steel containers. Laboratory gas chromatography was later performed on both gases collected from the yellow and white hydrate fabrics [13]. While similar, the yellow hydrate was slightly more enriched in heavy hydrocarbons, such as ethane, propane, and butanes. In addition to obtaining the gas composition, the core dissociation in the gas funnel allowed for volume estimates of the gas evolved. Both white (Figure 3a) and yellow (Figure 3c) hydrate cores were inserted into the gas funnel. The initial images allow for estimates of the overall core volume. Following complete dissociation of the hydrate using the heater, the gas evolved was contained in the top of the funnel for both the white (Fig. 3b) and yellow (Fig. 3d) hydrate cores. The volume of gas was later estimated by matching the images with measured volumes of water in the laboratory.

For the white hydrate core, the gas head space was 125 ± 5 mL. With a calculated in situ gas density of 5.06 mol/L, the head space contained 0.63 ± 0.03 mol of gas. The total core volume was 103.5 ± 3.3 mL. The gas evolution if the core was pure hydrate (51.07 mol/L, n = 6.3) is 0.73 ± 0.02 mol of gas. As no condensate was present in the white hydrate, the most likely explanation for this discrepancy is porosity in the hydrate, with pore space filled with either water or gas. This is in agreement with the small gas bubbles observed while coring the white hydrate. The minimum porosity, if the pores were only filled with water, is 13.1%. The maximum porosity, if the pores were only filled with gas, is 46.8%. Based on previous work, it is likely a combination of gas and water in the pores resulting in a porosity between 13.1-46.8%.

For the yellow hydrate core, the gas head space was 120 ± 5 mL. At in situ conditions, the gas density was calculated based on the measured composition to be 5.94 mol/L, corresponding to 0.71 ± 0.06 mol of gas. In addition to gas, a layer of condensate oil was present at the gas/liquid interface when the yellow hydrate was dissociated. Based on the thickness of this layer, the amount of condensate in the core was estimated to be 11.4 mL. The total volume of the hydrate core was determined to be 111.9 ± 3.8 mL. The yellow hydrate has a calculated hydrate density of 50.87 mol/L and hydration number (n) of 6.4. Using the total core volume less the condensate, the calculated gas evolution is 0.70 ± 0.03 mol of gas. There is excellent agreement between the moles of gas evolved and calculated moles in the hydrate core. This indicates that the yellow hydrate has very low porosity and likely
consists of solid hydrate with condensate distributed throughout the core. This agrees well with the relative difficulty in coring this hydrate. While we show a yellow hydrate core with low porosity, previous work on recovered samples of oil-stained hydrate from this area estimated from gas evolution that 76% of the water in the sample was hydrate [10]. The difference could be explained by the known presence of ice in the recovered samples (an artifact of recovery) and/or simply that these hydrates form in a heterogeneous way and porosity varies.

Hydrate dissolution rates
Both a yellow and a white core were injected into the open mesh container and mounted on the time-lapse camera frame. Figure 4 shows the mesh container with the hydrate cores inside at the beginning of the experiment. Changes in the hydrate core diameter were measured for both hydrate fabrics. Figure 5 shows the diameter of each specimen as a function of time. From a linear regression of the rate of diameter change over time, the yellow hydrate was found to be shrinking at a rate of 45.5 nm/s. For the white hydrate, the diameter was shrinking at a rate of 67.7 nm/s. The white hydrate was dissolving around 33% faster than the yellow hydrate. Because these hydrate had comparable compositions, the solubility driving force for both hydrate cores was similar. One possible case for the difference in dissolution rates could be the observed higher porosity in the white hydrate. Higher porosity would serve to increase the observed dissolution rate. Both rates are slower than the synthetic methane dissolution rate of around 94 nm/s. Solubility differences and external forces, such as currents speed, make direct comparison difficult. However, the rates are very similar between the natural samples and the synthetic sample, indicating that convective mass transfer was controlling the dissolution in this work.

If considering the calculated retreat rate of an exposed hydrate face, the dissolution rate would correspond to half of the measured diameter shrinkage rate. From this we obtain for the yellow hydrate a retreat rate of around 0.7 m/yr and around 1.1 m/yr for the white hydrate. Even with the slower rate of 0.7 m/yr, the retreat rate of exposed natural hydrate since the initial photographs in 2002 would be over 3.5 meters. Due to the similarities between photographs taken over the four year period, it is probable that other factors are contributing to stabilizing the hydrate against rapid dissolution. One of the most likely explanations is upward flux of methane-rich fluids. If mass transfer is controlling, the dissolution rate is proportional to changes in the gas saturation of the bathing fluid.
Figure 5 Linear regression of the hydrate core dissolution as a function of time.

CONCLUSIONS
Hydrate dissolution experiments were performed on naturally occurring hydrates at Barkley Canyon. Unlike controlled synthetic experiments, two hydrate fabrics were observed with very different characteristics, from porosity to association with a light condensate phase. Analysis of time-lapse images of the two hydrate fabrics showed that both dissolved at rates similar to a previous synthetic hydrate experiment, indicating mass transfer control. Future work is needed to understand the other complex features contributing to the stability of these seafloor hydrates.

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