An Experimental Determination of Natural Clathrate Hydrate Dissolution Rates in the Deep Sea

E.T. Peltzer [1], P.M. Walz [1], P.G. Brewer [1], R.M. Dunk [1], K.C. Hester [2], E.D. Sloan [2]

1. Monterey Bay Aquarium Research Institute, Moss Landing, CA 95039
2. Center for Hydrate Research, Colorado School of Mines, Golden, CO 80401

MR43A-1067

ABSTRACT:
In August of 2006 we carried out a series of geochemical experiments on the massive Structure II hydrate mounds in Barkley Canyon using MBARI's ROV *Tiburon* deployed from the R/V *Western Flyer*. One of the primary questions regarding the fate of this hydrate exposure at 860m depth is the temporal persistence of the un-sedimented surfaces exposed to steady currents of seawater which are undersaturated with methane. Previous work on the dissolution rate of laboratory prepared methane hydrate (Rehder et al., 2004) showed diameter reduction rates of ~3 m/year. These formations appeared largely unchanged from the earlier descriptions and photographs contained in media reports released in 2002 and later (Chapman et al., 2004; Lu et al., 2005) leading us to speculate that these hydrates are far slower to dissolve. In order to quantify their dissolution rates, samples of the outcropping hydrate, both a pure white hydrate and a much harder yellow, oil-stained hydrate, were collected using an ROV operated coring device and hydraulically expelled into an open mesh container for time-lapse digital photography over the course of the next two days. By exposing these samples of natural hydrate to the flow of ambient seawater we hoped to observe the dissolution rate consistent with the prevailing *in situ* environmental conditions. Initial analysis of the time-lapse photographs obtained using a Nikon Coolpix camera revealed an apparent diameter reduction rate for the yellow hydrate of approximately 0.043 $\mu m \cdot s^{-1}$, corresponding to a volume loss rate of $1.3*10^{-6}$ $cm^3 \cdot cm^{-2} \cdot s^{-1}$. The observed dissolution rate of the white hydrate was significantly faster, consistent with the observed large-scale undercutting of the exposed layered structures. Assuming that the yellow hydrate has a density of 0.93 g/cc and an average hydration number near 6, this yields a guest gas loss rate of about $9.4*10^{-9}$ $mol \cdot cm^{-2} \cdot s^{-1}$. This is approximately one-fourth the rate that was observed for the dissolution of synthetic Structure I methane hydrates under similar conditions in Monterey Bay. Thus the lifetime of the exposed surfaces must be short unless there is some form of active expulsion of fresh hydrates taking place or some mechanism that protects the hydrates from dissolution.

OBJECTIVE:
The objective of this experiment was quite simple. We wished to reproduce, using specimens of naturally occurring gas hydrate, an experiment previously conducted in Monterey Bay (Rehder et al., 2004), where we used time lapse photography to document the slow dissolution of hydrates in seawater. The Barkley Canyon hydrate outcrops are ideal for this purpose as they present two distinct layers (white and yellow) that have minor differences in composition, although both are structure II hydrates. It will be interesting to see how the different compositions affect dissolution rates, and how these compare with our earlier results with structure I hydrates.

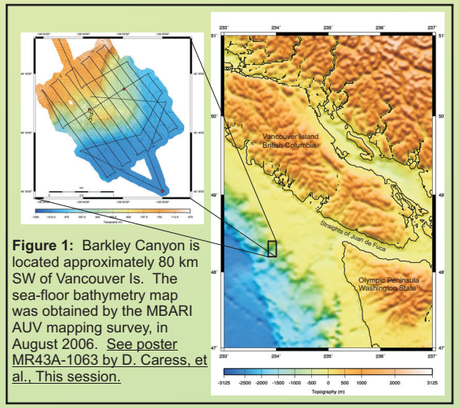

Figure 1: Barkley Canyon is located approximately 80 km SW of Vancouver Is. The sea-floor bathymetry map was obtained by the MBARI AUV mapping survey, in August 2006. See poster MR43A-1063 by D. Caress, et al., This session.

EXPERIMENTAL:
In order to observe the slow dissolution of a methane hydrate in seawater at Barkley Canyon, we elected to use time-lapse photography. This technique had worked well for us before when observing the slow dissolution of synthetic hydrate specimens in Monterey Bay. In addition to providing a well documented record of high resolution (3 mega-pixel) images, it would also allow us to use the ROV for other work elsewhere at the same time.

Prior to the beginning of the Barkley Canyon Expedition, we invested several days setting up and testing the hardware in the MBARI test tank. We used a small piece of white styrofoam as a synthetic hydrate specimen to simulate the high reflectance and subtle texture of the natural hydrate specimens. This set-up and testing of the hardware was necessary in order to properly adjust the exposure and focus of the camera. We also needed to determine the optimum time lapse interval in order to achieve the maximum number of data points without draining the camera battery excessively prior to the end of the anticipated experiment time period. This information was then used to pre-program the time lapse camera system prior to deployment. An interval of 10 minutes was chosen as the best compromise between frequent images and the need to collect data over the course of 60 hours.

Because much of the ROV payload was consumed by DORISS (MBARI's Deep Ocean Raman In Situ Spectrometer), the time lapse camera was deployed using a benthic elevator (Figure 3). Immediately prior to deployment, the time lapse program was initiated. Because of the steep terrain near the hydrate outcrops, and not wishing to lose the elevator down the axis of Barkley Canyon, we lowered the elevator on the deep-sea hydrowire and used an acoustic release to drop it within about 25 meters of the hydrate mounds. In this way the elevator would be nearby where the samples were collected, but not so close as to get in the way of the ROV nor so close that the ROV operations would interfere with the experiment.

Once the camera was positioned on the sea-floor, we dove the ROV to the sea-floor and proceeded to collect hydrate specimens from a nearby outcrop. Samples were cored from the outcrop using a specially constructed stainless steel coring device. The leading edge of the corer had a serrated rim much like a hole-saw. Inside the corer was a hydraulic ram to eject the hydrate core. Samples were collected using the ROV manipulator arm (Figure 2), then after a short run from the outcrop to the elevator, the specimens were ejected into the open mesh exposure container (Figure 4). Specimens of both the yellow and white hydrates were obtained in this manner.

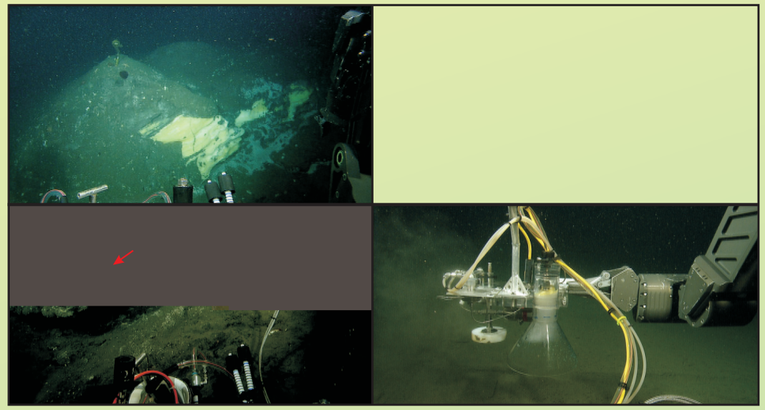

Figure 2: Numerous hydrate sites such as this one (upper left) were found at Barkley Canyon. Core sampling was performed using a stainless steel cylinder with serrated teeth (lower left). The repeated twisting motion of the manipulator arm was sufficient to slowly cut into the hard yellow hydrate material when pressure was applied normal to the axis of rotation. A hydraulic ram inside the stainless cylinder was used to eject the cored material into a plastic funnel (upper right) containing a 240 VDC 400 watt heating element. Heating the hydrate core *in-situ* enabled us to dissociate the solid hydrate to gas (bottom right). The yellow hydrate decomposition also yielded a small amount of lightweight yellow colored oil. The gas was then collected inside 150 ml evacuated stainless steel cylinders. The red arrow indicates the core hole from an earlier core sample. Table 1 shows the results of the GC analysis of the collected gases.

EXPERIMENTAL: (continued)
Using the same hydrate coring technique, we were also able to collect hydrate samples and melt them in our heated gas collection funnel (Figure 2). Once the hydrates were thermally decomposed, the evolved gases were collected into evacuated stainless steel containers. These gas samples were then returned to MBARI and analyzed by gas chromatography (Table 1).

Table 1: GC Analysis of Gases from Melted Hydrates

	White Hydrate (Mol %)	Yellow Hydrate (Mol %)
Methane	86.20	76.97
Ethane	7.04	10.65
Propane	3.01	7.87
i-Butane	0.52	1.10
n-Butane	0.61	0.69
Neopentane	0.14	0.13
i-Pentane	0.12	0.09
n-Pentane	0.09	0.08
$N_2 + O_2$	0.50	0.15
CO_2	0.09	0.50
Totals	98.31	98.23

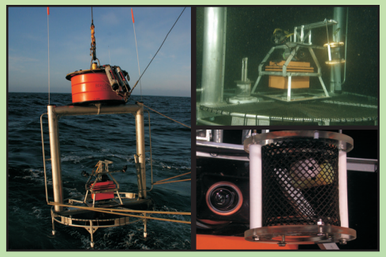

Figure 3 : Time Lapse Camera system attached to MBARI benthic elevator for deployment and transport to the sea-floor (left). Closeup views of camera with lights on to take an image (right-top) and an extreme close-up of the two hydrate core specimens (right-bottom).

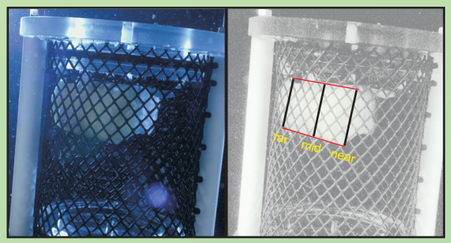

Figure 4: Open mesh chamber containing hydrate cores. Right image illustrates core measurement method. Three lines across the core (far/mid/near) were scaled to the known dimension (3/4" dia.) Of the white rod seen at the left side of the chamber.

RESULTS:
The diameters of the two hydrate specimens are plotted as a function of time in Figure 5. The slope of the linear regression line equals the apparent diameter reduction rate. While we had hoped to obtain data for both specimens, it is obvious from Figure 4 that the yellow hydrate core blocked our view with the time lapse camera of the white hydrate core. Because this was observed at the time, we also took digital photographs of the hydrate exposure chamber using the Nikon Coolpix camera on the ROV (Figure 3) from time to time in order to have some data for the white hydrate specimen. While this time series was not nearly as detailed as the one obtained from the time lapse camera for the yellow hydrate, it was sufficient to allow us to estimate to a first approximation, the dissolution rate of the white hydrate. Since the hydrate core is dissolving from all sides, the apparent diameter reduction rate is twice the erosion rate for a single exposed surface.

From our regression analysis we determined that the yellow hydrate diameter was shrinking at the rate of 45.5 nm/sec, and a single surface was dissolving at the rate of 22.8 nm/sec. At that rate, an exposed surface will retreat approximately 0.7 m in a year. For the white hydrate, we observed the core diameter decrease of 67.7 nm/sec or a single surface dissolution rate of 33.8 nm/sec, about 50% faster than the yellow hydrate. An exposed surface of white hydrate will retreat approximately 1.1 m per year. If the two surfaces are exposed simultaneously, with the yellow hydrate overlying the white -- as we see in Figure 2 -- than an overhang of 0.4 m can be produced in a single year assuming that the dissolution rates we observed for an exposed core are appropriate for the erosion of the face of the hydrate outcrop.

In our previous study of the dissolution rate of synthetic methane hydrates in Monterey Bay (Rehder et al., 2004), we observed diameter shrinking rates of about 94 nm/sec. There are several factors that could account for this difference: for example, current velocity and temperatures are different, making it hard to make a direct comparison; the synthetic hydrates were structure I and were compacted mechanically from granules, while the natural hydrates were structure II and appeared to be a continuous massive block; and compositionally the synthetic hydrates were prepared from methane only, the natural ones were a complex mixture of gases.

Based upon the observed dissolution rates, we can calculate the rate of gas released from the dissolving hydrates. At 22.8 nm/sec, 5.6 * 10^3 moles of gas / m^2 / yr from the yellow hydrate. For the white hydrate, dissolving at the rate of 33.8 nm/sec, 8.3 * 10^3 moles of gas is released per m^2 of exposed hydrate per year.

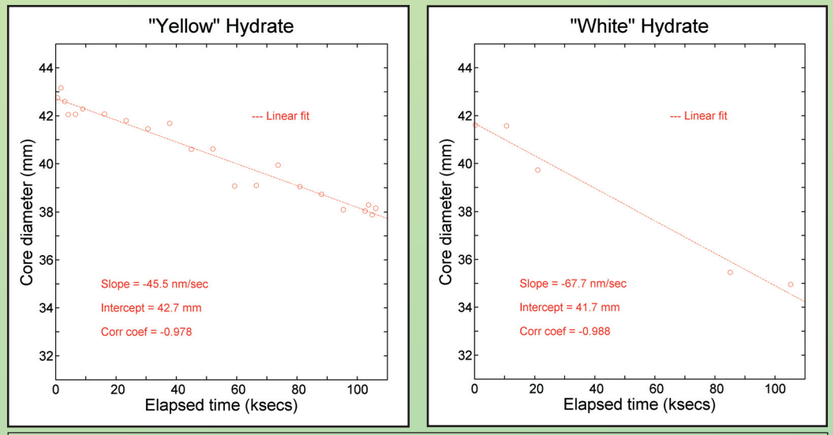

Figure 5: Regression analysis of the hydrate core dissolution. The diameters of the yellow hydrate core (left) and the white hydrate core (right) are plotted as a function of time. The slopes of the two regression lines equals twice the rate of surface erosion since the core is dissolving on all sides. The y-intercept equals the diameter of the cores at the time of the initial exposure.

REFERENCES:
Chapman et al. (2004). Eos, Trans. Amer. Geophys. Union. 85: 361, 365.
Lu et al. (2005). J. Geophys. Res. 110: B10204, doi:10.1029/2005JB003900.
Rehder et al. (2004). Geochim. Et Cosmochim. Acta 68: 285–292.

ACKNOWLEDGEMENTS:
The authors would like to thank the David and Lucille Packard Foundation, the U.S. Dept. of Energy (DoE) and the National Oceanic and Atmospheric Administration's National Undersea Research program (NOAA/NURP) for their support of this work. We also thank the captain and crew of the R/V Western Flyer and the pilots of the ROV Tiburon: we could not have accomplished this research without their assistance and participation.

For a pdf copy of this poster (11" x 17") contact: Ed Peltzer (email = etp3@mbari.org)