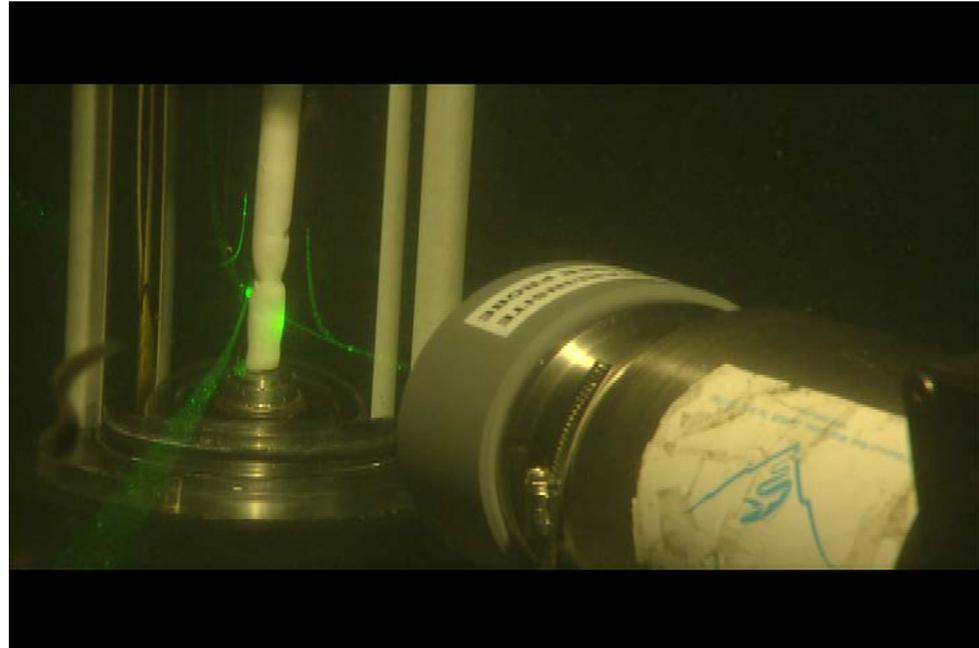


Advances in Executing Complex Geochemical Experiments on the Sea Floor: $\text{CH}_4 \rightarrow \text{CO}_2$ Hydrate Conversion as a Greenhouse Gas Strategy?



Peter G. Brewer
MBARI
WHOI Geodynamics Seminar
April 2013

An Energy Coup for Japan: 'Flammable Ice'

The New York Times



Gas flames from a burner on a deep-sea drilling vessel tapping methane hydrate in the Pacific off central Japan.

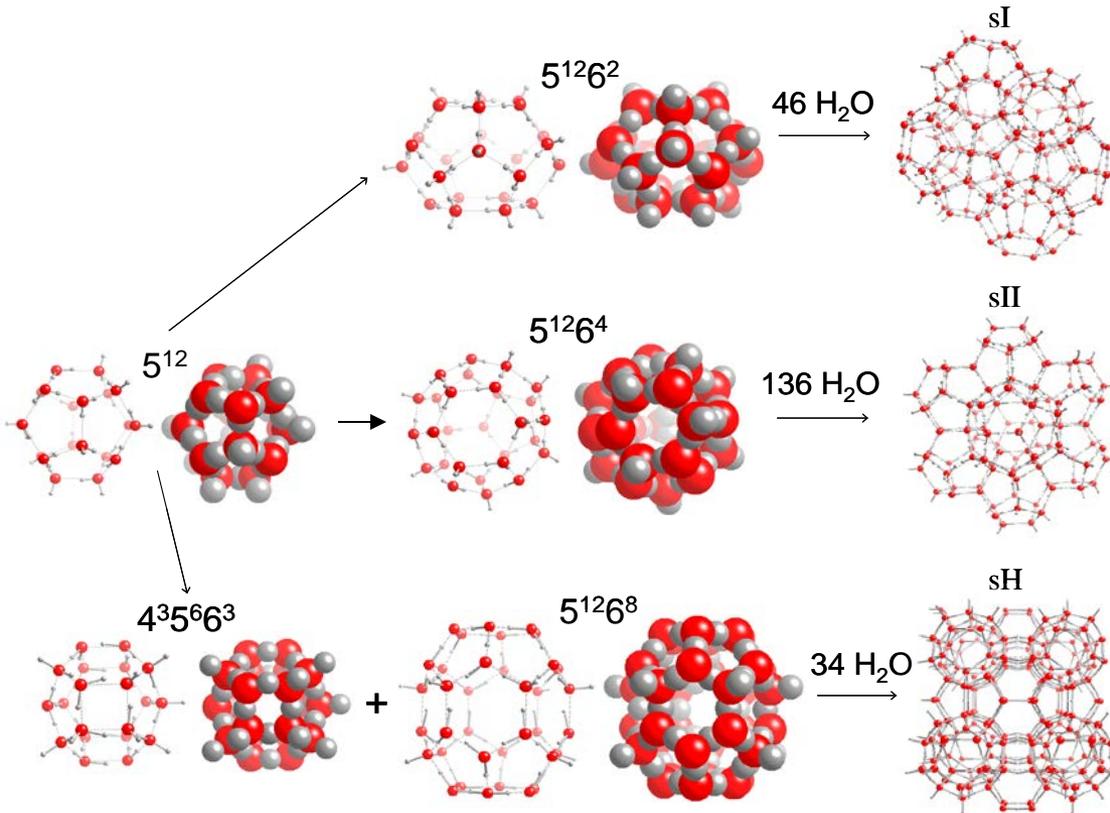
By [HIROKO TABUCHI](#) Published: March 12, 2013

A nice example – inadvertent demonstration of hydrate depressurization



What are hydrates? – and can the guest molecules swap?

The guest molecules are held within the cage by van der Waals forces: the water cage is formed by hydrogen bonds



- Inclusion compounds
 - Made of water cages
- Concentrates gases
- Form at $\uparrow P, \downarrow T$

To produce gas from hydrates we have to break the water cages to let the gas out – not everyone agrees with this statement!

Background – Recovery of free gas from hydrates

- **The standard approach** is de-pressurization. The problems are that the endothermic phase change cools the system and can form water ice – and that in order to achieve meaningful pressure reduction the formation waters must first be pumped off. This takes time and energy.
- **An alternate approach** was first suggested by Japanese scientists (e.g Komai et al., 2002) in using liquid CO₂ as a displacement agent, using the thermodynamically favored formation of CO₂ hydrate to sequester CO₂ as a solid, releasing CH₄ gas. The reaction was shown to proceed in a sandstone core e.g. Ersland et al., 2009.
- **The problems** are the slow rate of the reaction, the very high solubility of CO₂ in aqueous solution (10x that of typical gas), and the complex dynamics of the saturated boundary layer required to achieve success.
- **Hypothesis** – Other gases can effectively displace the water phase, and since immersion of the solid hydrate in a non-CH₄ gas phase creates the condition $\mu_{\text{hyd}} \neq \mu_{\text{gas}} \neq \mu_{\text{water}}$ then we can expect dissociation of hydrate to form a gas phase.
- **Experiment** – We have tested this in a sea floor field experiment

Some candid comments from Ko-ichi Nakamura on the Press Release:

“You may have already caught the news that JOGMEC as well as METI announced on Tuesday that they successfully made the first production of methane gas (in the world, they say) from the strata below the seafloor. It was a kind of impatient press release because that the day was the first day when the ignition flare started at the outlet of a pipe from the hole on the drilling vessel Chikyu. The production test is planned to be completed within this month so that I had expected that the announcement would be at least later than several days before the end of this month when they need to wrap up all the equipment. You may have known that the **gas production in the 2007 Malik production test ended 12.5 hours after the start.**

Nevertheless, the minister of METI said on the TV that they are aiming to proceed to the next R&D step for the commercial production starting within five years.”

So what is the mechanism at work, and why might it come to an end as gas is withdrawn?

Replacement of Methane from Quartz Sand-Bearing Hydrate with Carbon Dioxide-in-Water Emulsion

Xitang Zhou,^{†,§} Shuanshi Fan,^{*,‡} Deqing Liang,[†] and Jianwei Du[†]

Because of the difference in chemical affinity of CO₂ versus CH₄ in the structure I (sI) hydrate structure, the mole fraction of CH₄ would be reduced to approximately 0.48 in the hydrate and rise to a value of 0.7 in the gas phase at equilibrium. Using a Raman spectroscopic method, Uchida et al.¹³ confirmed the guest molecule swapping reaction at the solid–gas interface.

Can we beat the system? Some seem to think so

“guest swapping as a mechanism”

The data obtained from lab pressure vessel experiments suggested to investigators that some form of spontaneous “guest swapping” of molecules into the hydrate cages occurred, with no intervening cage opening and liquid water formation. This seems unreal.

SPE 102915 2006

Magnetic Resonance Imaging of Methane - Carbon Dioxide Hydrate Reactions in Sandstone Pores

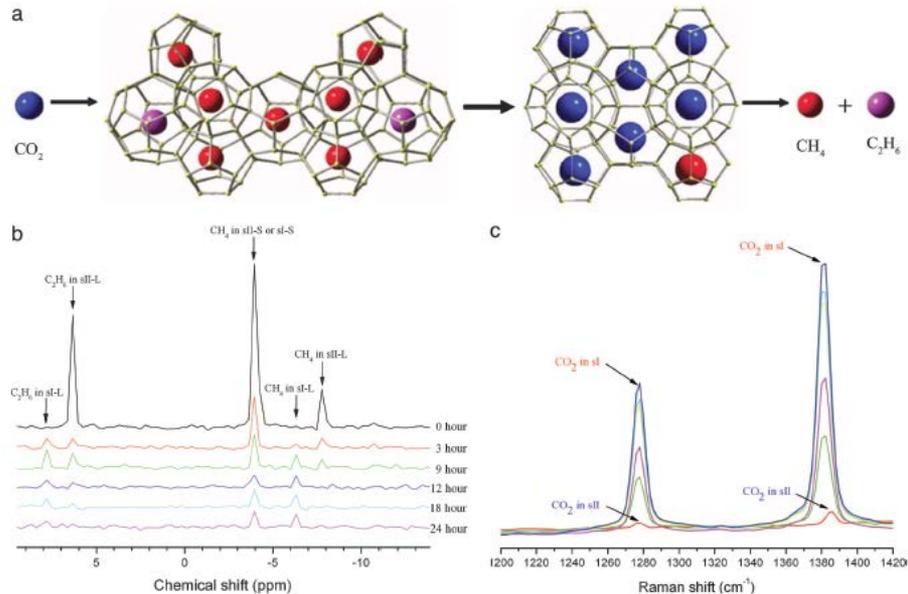
Graue, A., Kvamme, B. /U. of Bergen, Baldwin, B.A. /Green Country Petrophysics LLC, Stevens, J., Howard, J. /ConocoPhillips, Ersland, G., Husebø, J. /U. of Bergen, Zornes, D.R. /ConocoPhillips

during hydrate growth. Experimentally it was verified that methane hydrate in porous sandstone spontaneously converted to CO₂ hydrate when exposed to liquid CO₂ at high pressure and low temperature. It has experimentally been determined that without heating, an exchange process between CO₂ and methane occurred allowing the injected CO₂ to be stored as hydrate resulting in spontaneous production of methane, with no associated water production. The MRI images provided

“spontaneous production with no associated water production”

Sequestering carbon dioxide into complex structures of naturally occurring gas hydrates

Youngjune Park*, Do-Youn Kim**†, Jong-Won Lee‡, Dae-Gee Huh[§], Keun-Pil Park[§], Jaehyoung Lee[§], and Huen Lee*†



“Through an ocean-storage cycle scenario either a relatively pure CO₂ or a mixed CO₂ stream can be successfully sequestered irrespective of complex structures of CH₄ hydrate deposits.”

The “spontaneous” exchange was further pressed by Park et al. (2006) who advocated displacement by a CO₂-N₂ gas mixture and claimed that flue gas-like streams could convert SII (CH₄-C₂H₆) hydrates. We chose to experimentally test this in a sea floor experiment.

A quick word on Raman data: Example spectrum from a Cascadia hydrate showing a well-resolved complex mixture of hydrates from C1 to C4 with cage occupancy etc.

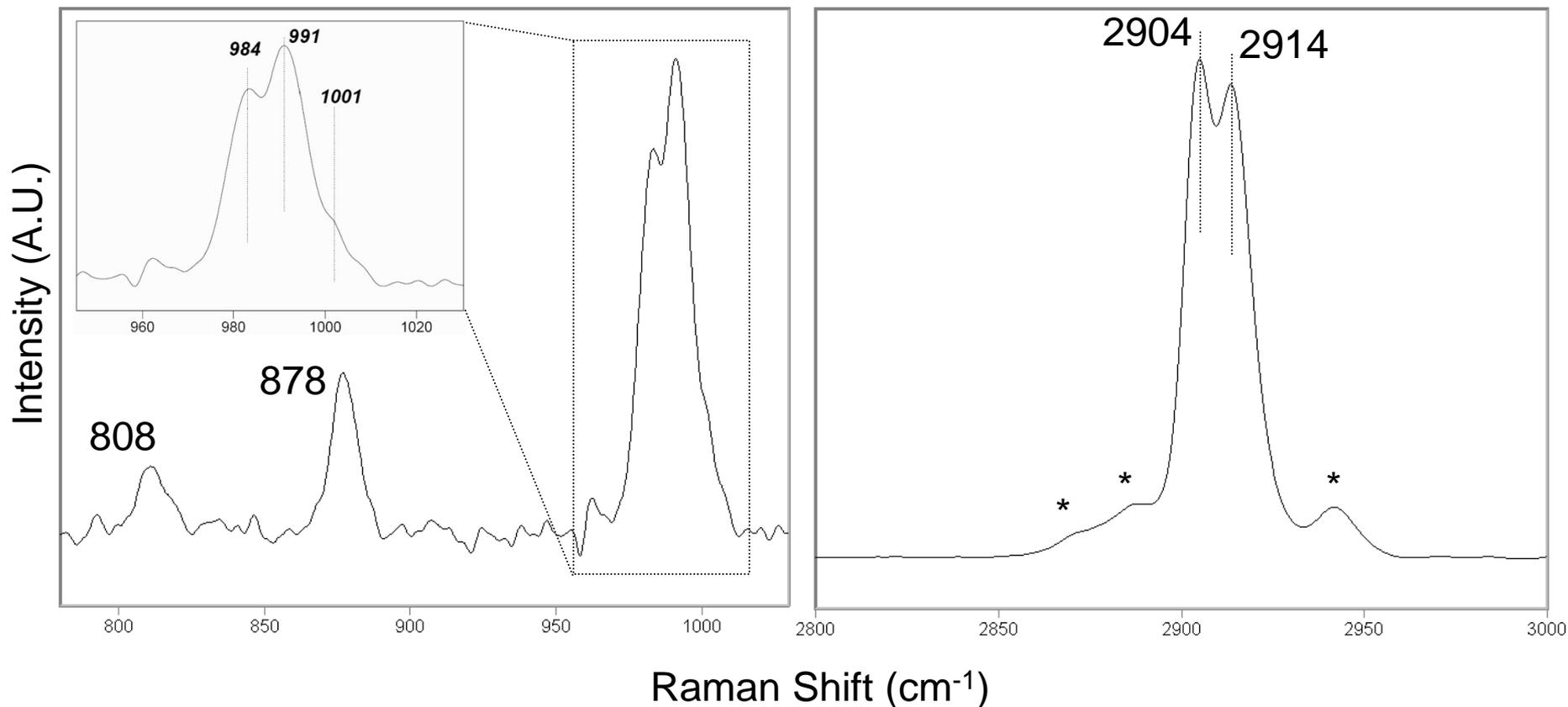


Fig. 7: Representative Raman spectrum from natural hydrate at Barkley Canyon (8.5 MPa, 278 K, collection time: 150 s). Peaks labeled at 808 cm⁻¹ (i-C₄H₁₀ ν₇, sII 5¹²6⁴), 878 cm⁻¹ (C₃H₈ ν₈, sII 5¹²6⁴), 984 cm⁻¹ (SO₄²⁻, dissolved), 991 cm⁻¹ (C₂H₆ ν₁, sII 5¹²6⁴), 1001 cm⁻¹ (C₂H₆ ν₃, sI 5¹²6²), 2904 cm⁻¹ (CH₄ ν₁, sI/sII large cage), 2914 cm⁻¹ (CH₄ ν₁, sI/sII small cage). Asterisks marked for the C-H stretching modes of C2+ molecules in the hydrate phase.

Why not try a simple experiment to test some of these ideas?

A Sea Floor Methane Hydrate Displacement Experiment Using N₂ Gas



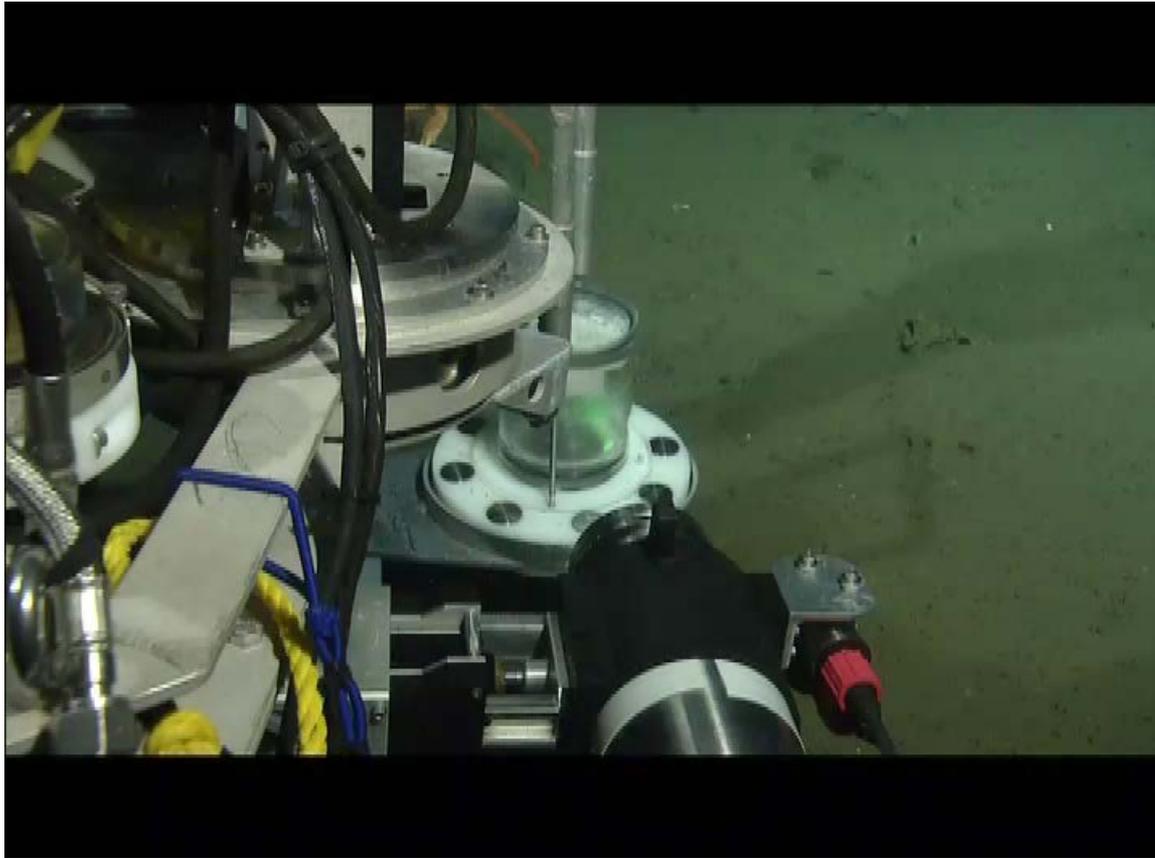
Peter G. Brewer¹, Edward T. Peltzer¹, Peter M. Walz¹, Xin Zhang², and Keith Hester^{1,3}

1. Monterey Bay Aquarium Research Institute
2. Ocean University of China, Qingdao
3. ConocoPhillips, OK

We were curious as to how molecules could move in and out of cages without liquid water being formed – or how once a surface skin of a new guest hydrate was formed the larger mass could convert etc.

Earlier Work –

In 2006 we carried out a first field study of the CO₂ displacement reaction at the Barkley Canyon hydrate site using *in situ* Raman techniques to observe progress.

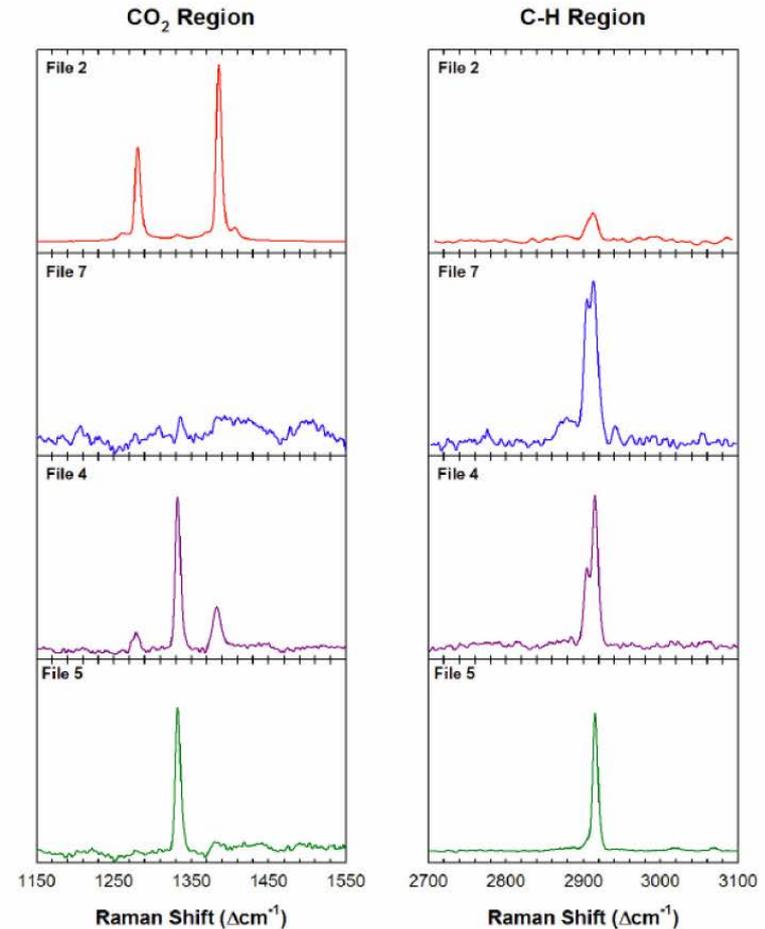


The experiment was non-ideal. The hydrate was Structure II, the reaction was slow, and frosting on the vessel window created a measurement challenge.

Results of the 2006 experiment:



The 2006 experiment was invaluable for creating technique in difficult sample acquisition and handling, and in spectroscopic measurement.



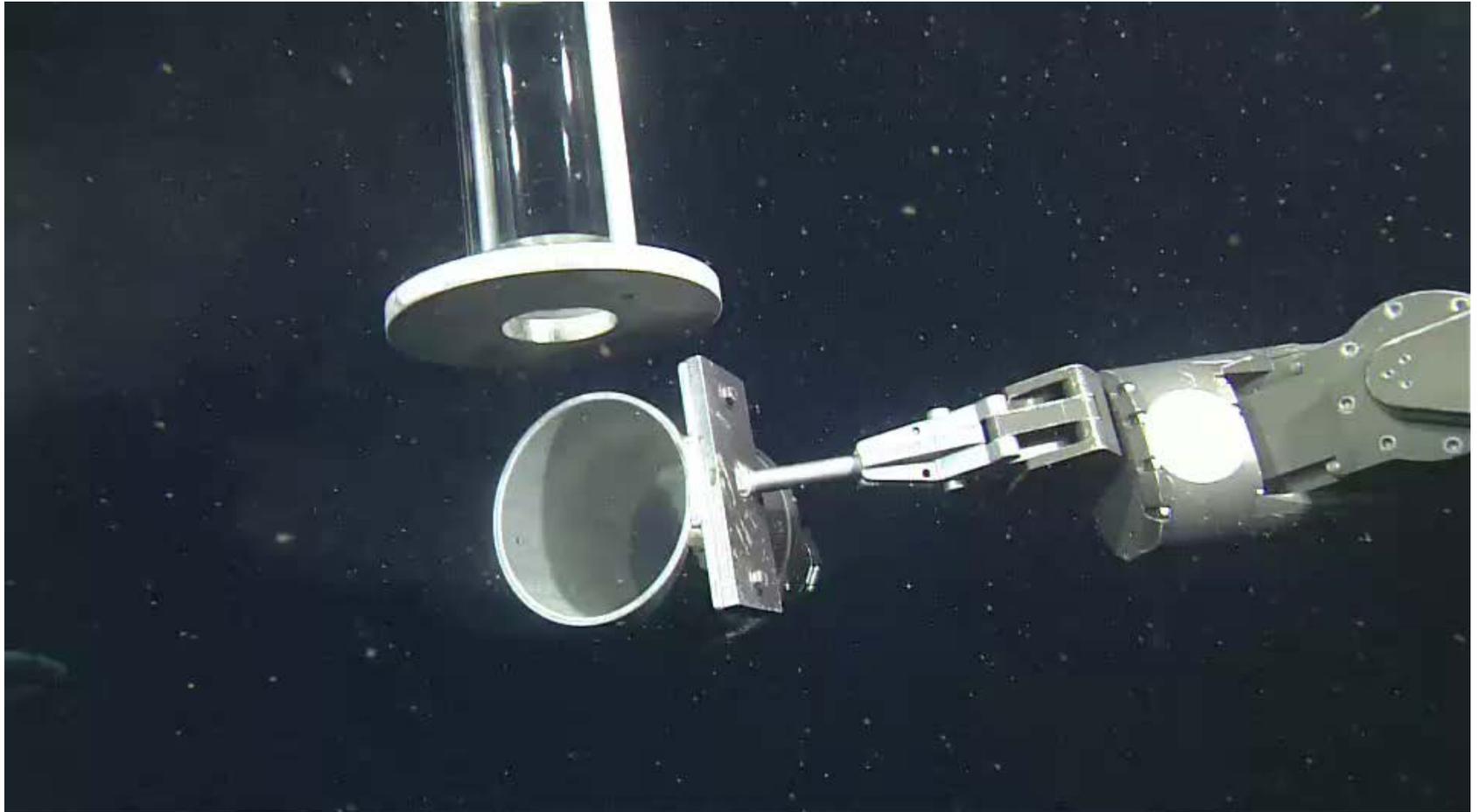
The results showed clear signals of free CH₄ gas, solid CH₄ hydrate, liquid CO₂, and CO₂ hydrate. But the reaction products were small and the observing mode through sea water and coping with CO₂ hydrate frosting on the glass walls was not ideal.

The site chosen was Hydrate Ridge South where SI hydrate is known to occur in surficial sediments:

The first challenge was to collect significant quantities of hydrate in a manner allowing their transfer to a reaction/measurement vessel:



The second challenge was to transfer the collected hydrate into the glass cylinder for the reaction and measurement sequence:



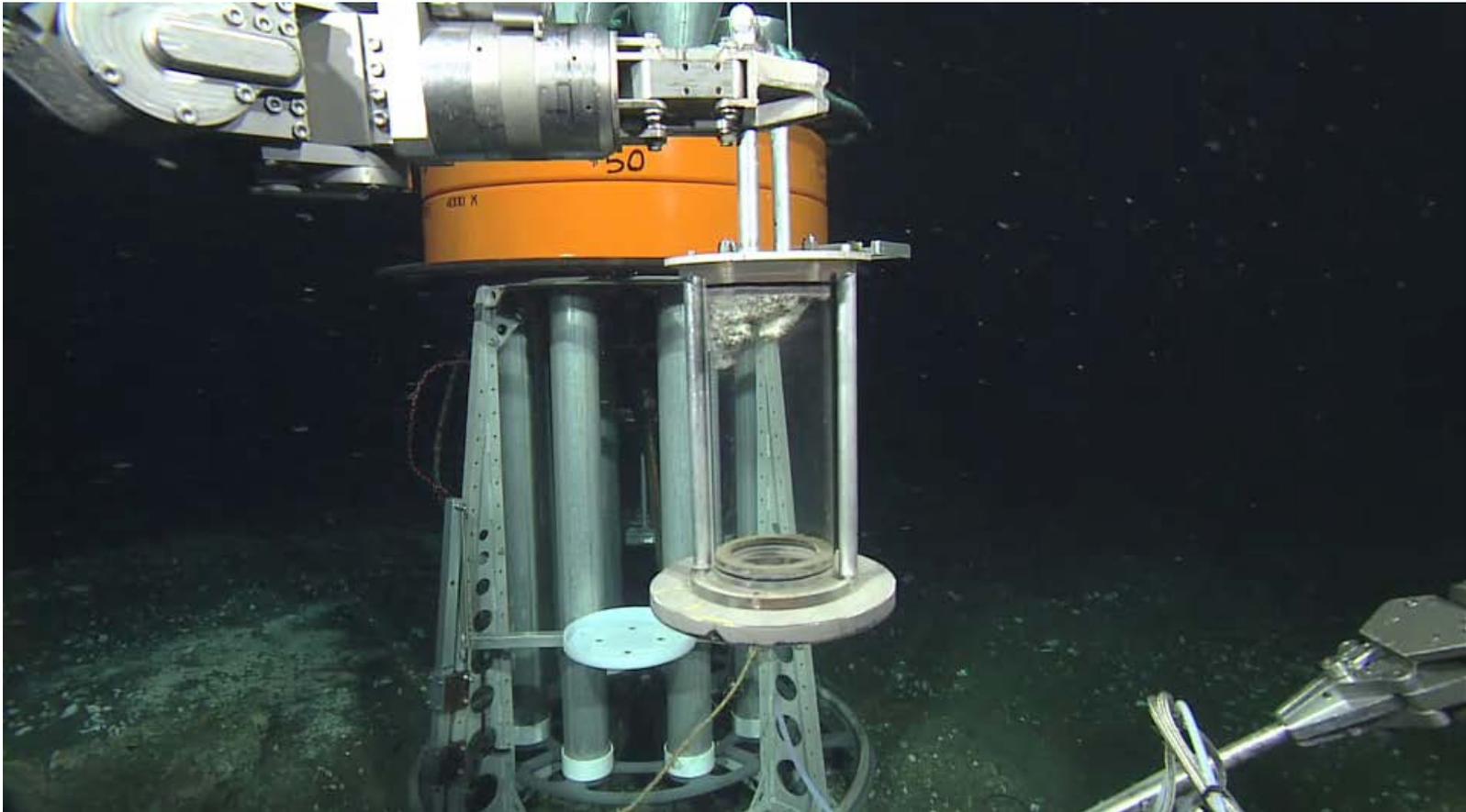
This was operationally the most delicate part of the entire operation

Experiment dimensions



The experiment used a glass cylinder 12.5 cm diameter, 30.5 cm high plus base for a volume of 3.72 liters. The contained hydrate amount is not known well, but, correcting for an estimated 50% porosity the volume is $\approx 200\text{cm}^3$, which could yield about 32 liters of gas at STP. This is approximately 1.4 moles CH_4 . The *in situ* conditions are $T = 4.22^\circ\text{C}$, $P = 8.0\text{ MPa}$, $S\% = 34.29$. The volume of CH_4 gas *in situ* is $\approx 350\text{ ml}$.

The vessel was charged with N₂ gas to about 50% volume



The experiment was set on a metal plate to inhibit mixing loss and left for 7 days.
The initial volumes were: Gas phase \approx 1.7 liters Water phase \approx 1.7 liters
Solid hydrate \approx 200 cm³

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The chamber with harvested hydrate was placed on a stand and left for two days while other work was done – we really had no idea of how fast the reaction would proceed or if the result would be measurable. A shot in the dark for scaling purposes and technique development.

Comparing the Before and After Images of the 7 day Experiment



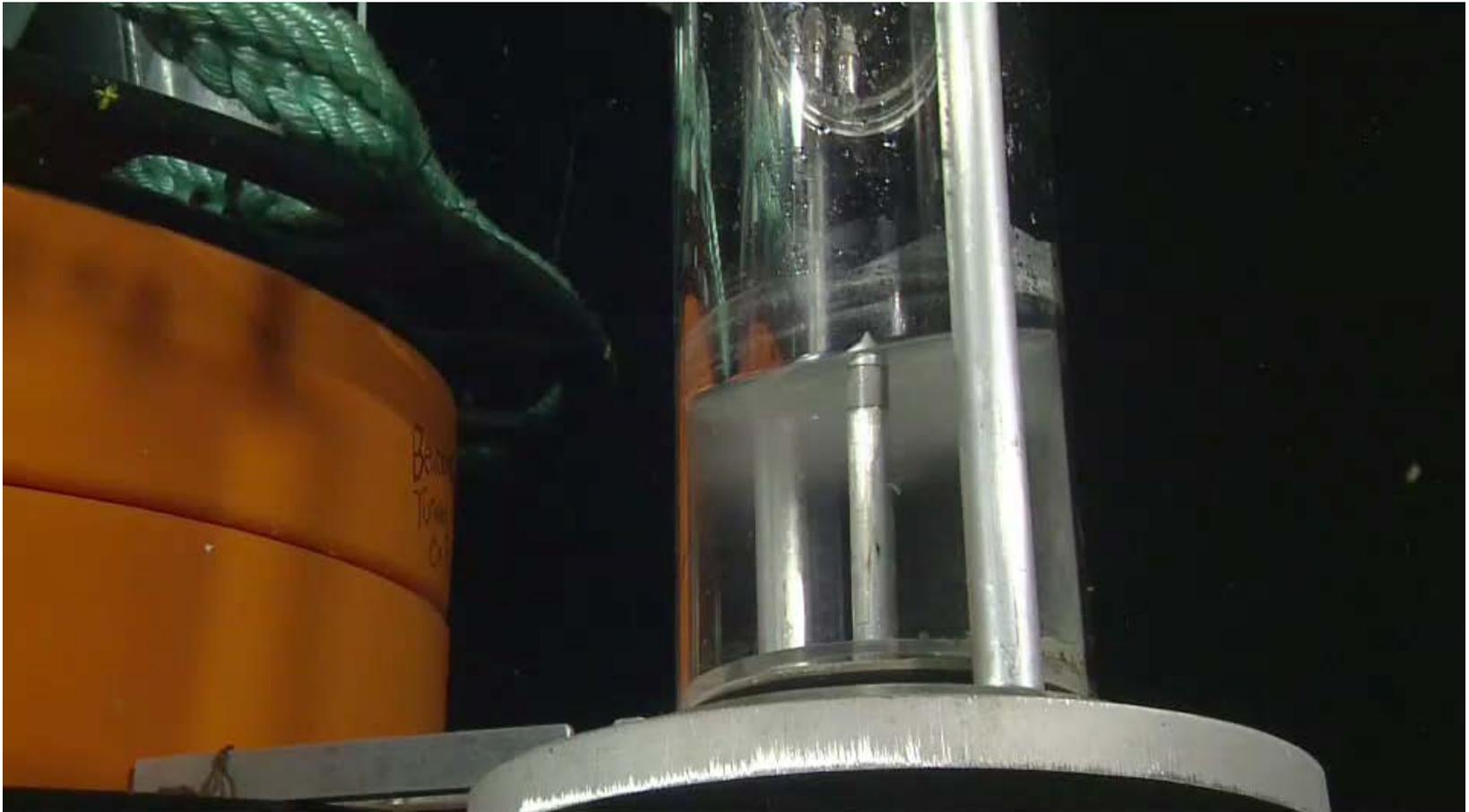
From image analysis the initial gas volume was 1.709 L. The final gas volume was 1.806 L. The increased gas volume has pushed some water out. The difference of 97 ml indicates gas produced, minus the amount dissolved in the water phase. A "bath tub ring" was left on the glass from adhering sediment in the hydrate fragments.

After hydrate decomposition the challenge is to measure the water and gas phases



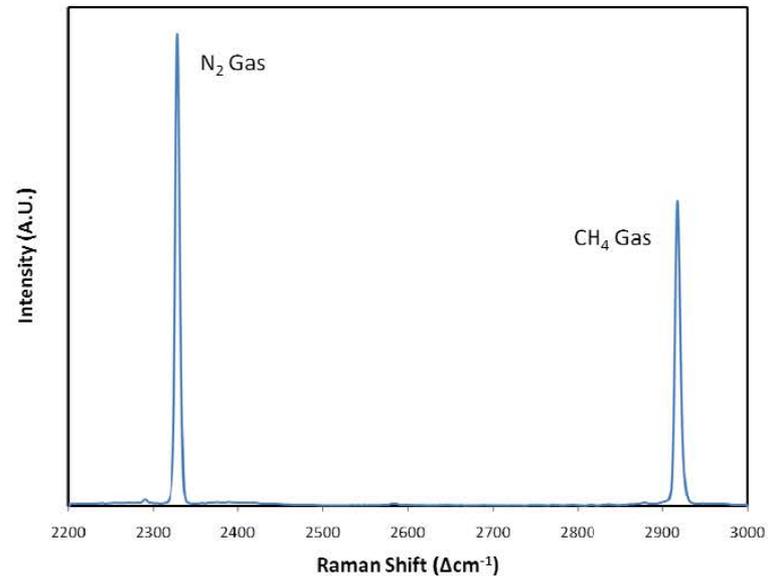
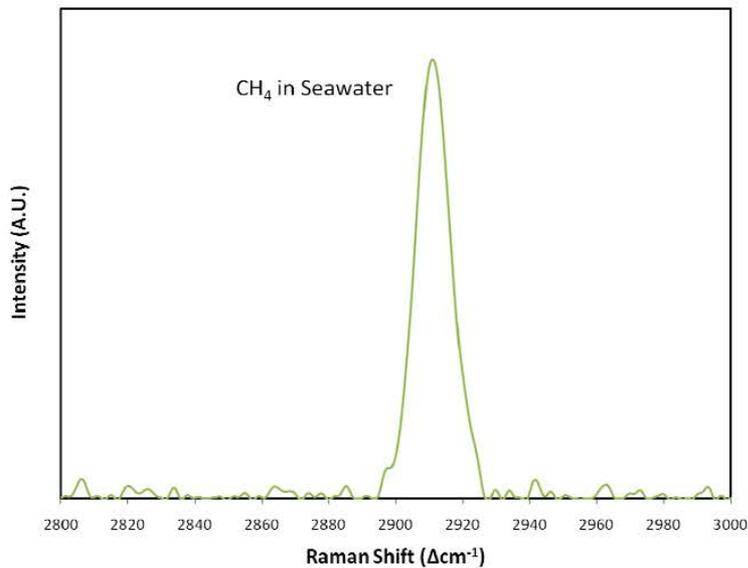
Hydrate decomposition releases fresh water, and cools the system. The heat dissipates, but the fresh water is trapped and the halocline layer, seen as a cloudy zone is where most of the dissolved CH_4 resides. We placed the sensor tip both below this layer (no signal) and in it, showing high dissolved CH_4

The gas phase signal was measured easily by moving the probe upwards



The moment at which the gas sample is sucked in can be seen in the change in reflectance of the filter frit as it goes from wet to dry. Only a very small volume is required for measurement.

The spectra show the dissolved CH_4 in the water phase in the freshwater halocline below the water-gas interface, and the primary N_2 and $\nu^1 \text{CH}_4$ peaks in the gas phase



The Raman cross section of CH_4 is about 9x that of N_2 – 4 bonds, and higher polarizability – so from the peak area ratios we calculate that the gas phase contained about 10% CH_4 gas. What is the limit we can expect?

Thermodynamic limits set by hydrate phase formation in N₂-CH₄ mixtures

For the conditions existing at the experimental site:

T = 4.22°C

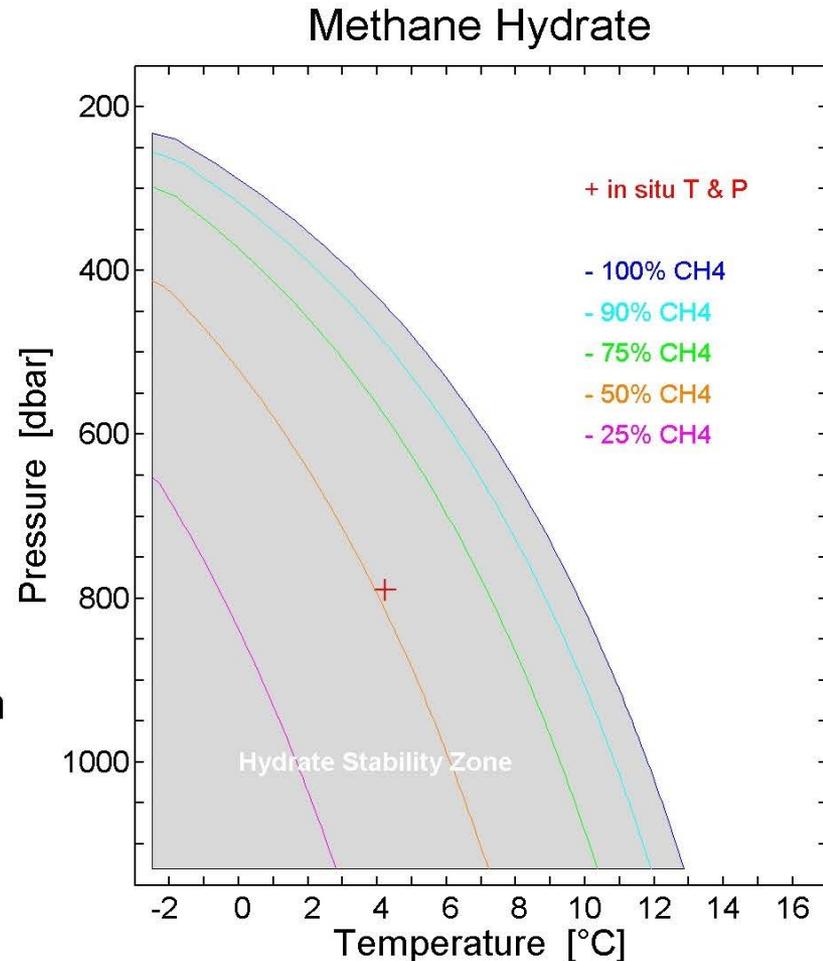
P = 8.0 MPa

S = 34.29

we calculate the phase limit to be about 53% CH₄ in the gas phase.

This novel form of hydrate displacement to gas appears to be rapid and well defined. Other gas mixtures can be tried.

It remains to be seen whether production of a 50% CH₄-N₂ gas mixture is commercially viable, or whether the technique is useful for flow assurance and hydrate plug removal.



A test of the Park et al.(2006) study by subjecting CH₄hyd to a N₂-CO₂ gas mixture

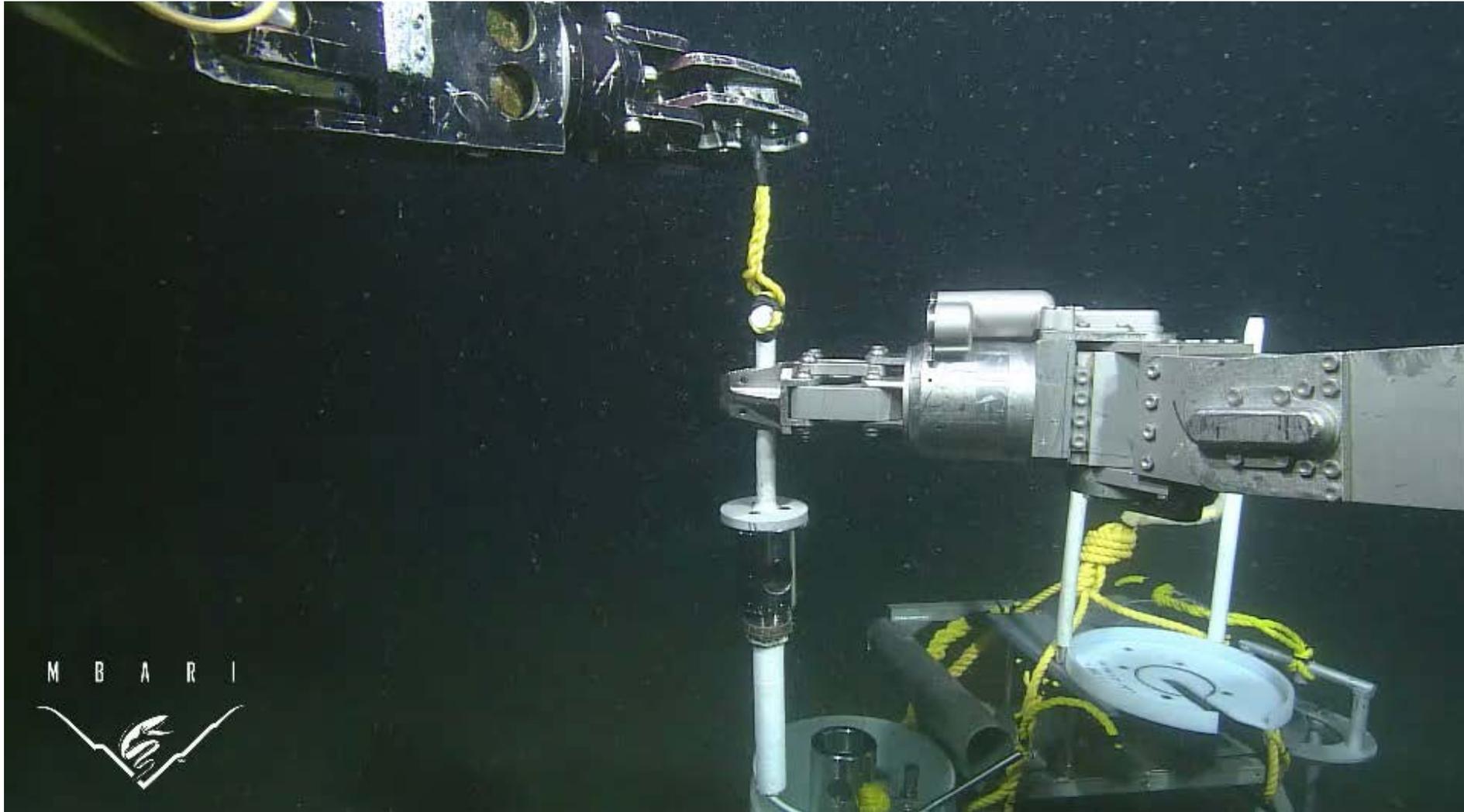


ROV *Ventana* ready for deployment. The laser Raman is lower center, to the right is the frame holding the glass experimental chamber, the white bucket holds the pressure vessel containing the hydrate, the N₂-CO₂ gas cylinder is stowed under the vehicle

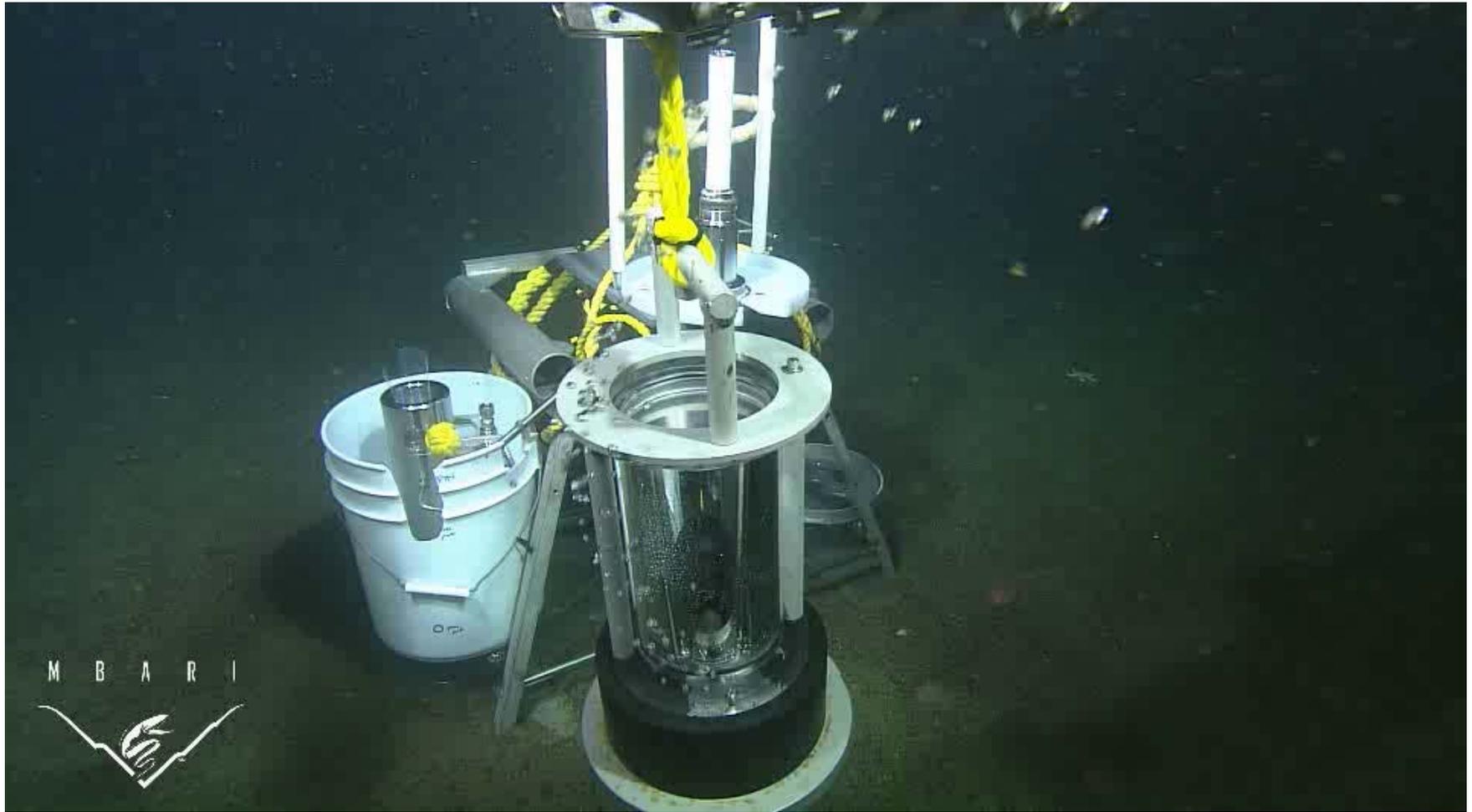
The first task was to open the valves and release the gas, pull the safety pin, and remove the hydrate sample



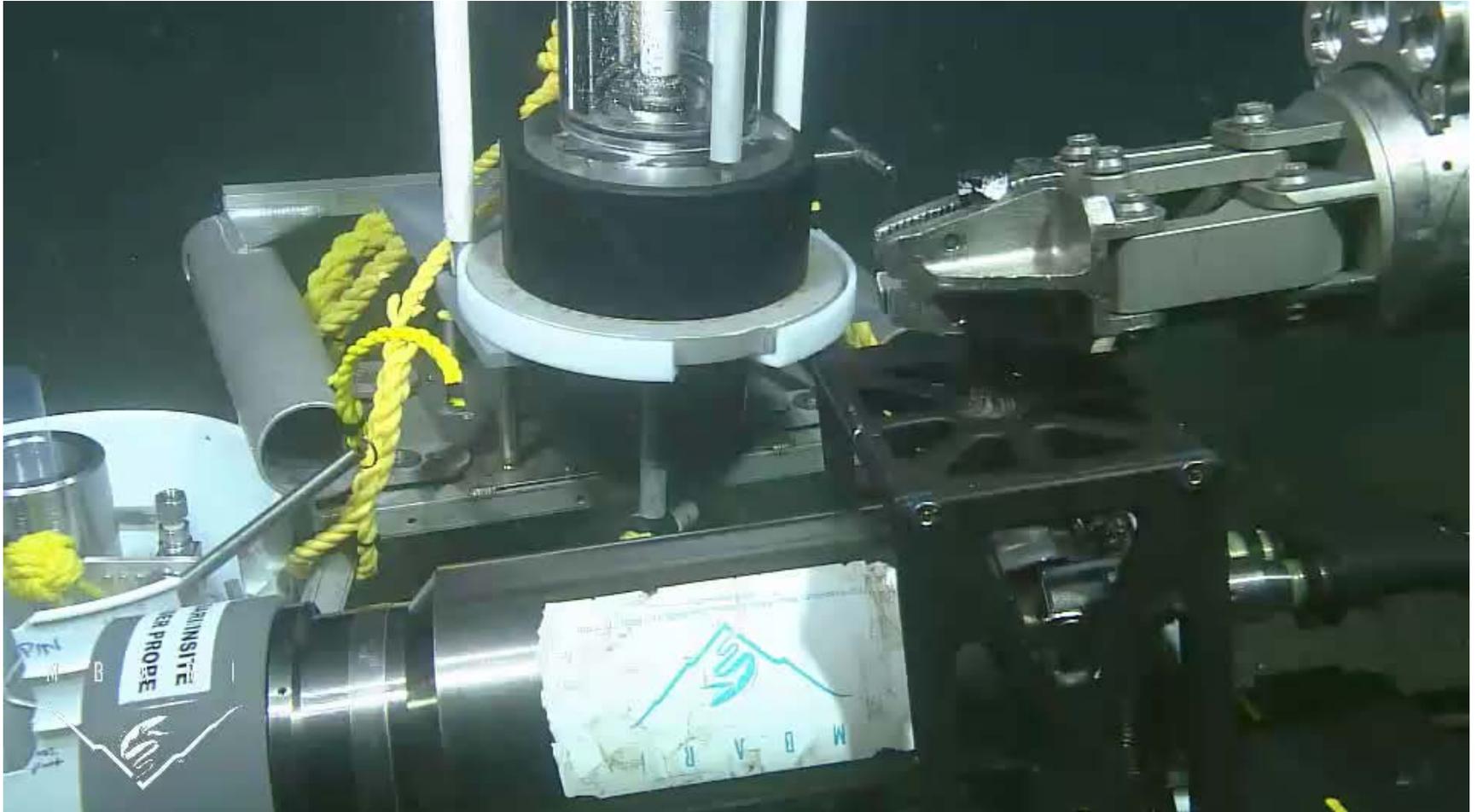
Next the hydrate had to be re-acquired and inverted to place on the stand. As soon as the hydrate is removed from the pressure vessel it will begin dissolving since oceanic p_{CH_4} is very low. Cannot waste any time here.



The glass experimental chamber had to be loaded with the N₂-CO₂ gas mixture – which would immediately begin dissolving into the exposed ocean water interface and fractionating with the more soluble CO₂ disappearing more quickly – time matters.



Acquire the Raman probe head, place in position, and focus either on the solid or the gas space and record the spectra over time. Changing gas chemistry? Changing solid hydrate?



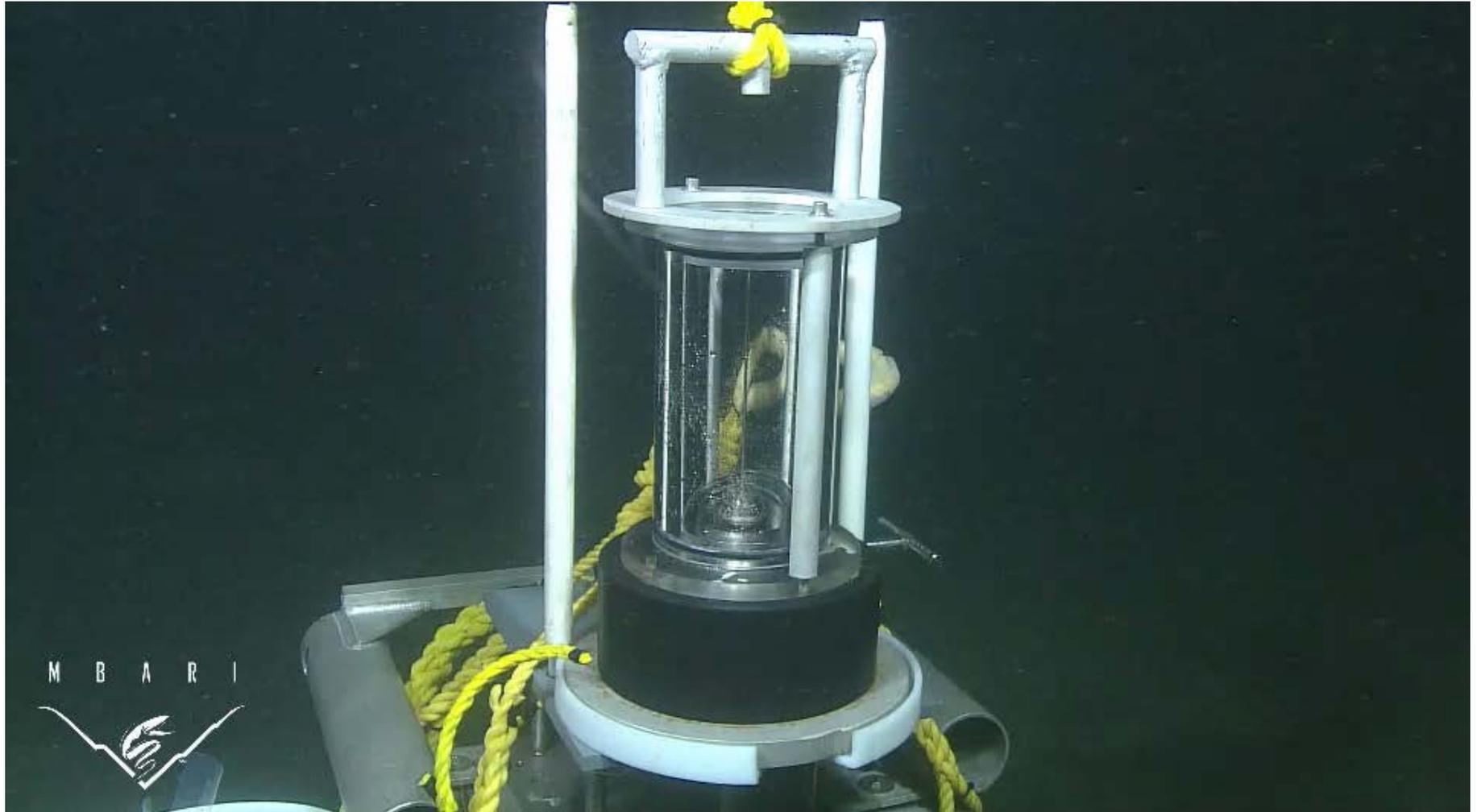
We turn the vehicle lights off to acquire spectra, and the probe head is heavy enough that positioning was a challenge. We can scan up and down the solid hydrate to see if there are any changes and CH₄ to CO₂ conversion as promised by some.



By the end of Day 1 – a couple of hours exposure the hydrate showed rapid loss of mass and preferential sublimation at local discontinuities. The surface appeared wet, and liquid water could be seen sliding down the surface – and surely dissolving the CO₂ gas. We did not see evidence of CO₂ hydrate formation in the spectra.



Day 2 – When we returned the next day all hydrate had gone – and must have done so quickly. We acquired the gas spectra, packed up, and came home.



Interpreting the spectroscopy data obtained in the field:

The problem is that of quantitatively deriving molar data from a changing ternary gas mixture under pressure. Each component has its own Raman cross section and in the case of CO₂ the signal appears as a Fermi dyad from accidental degeneracy.

The details: Make up standards and measure:

Gas Standard Fabrication and Processing. Four CH₄/N₂ mixtures of 0.10, 0.20, 0.30 and 0.40 mol ratios, and four CO₂/N₂ mixtures of 0.05, 0.10, 0.15, 0.20 mol ratios, were generated in 1500 psi stainless steel cylinders. Gas standard cylinders were filled to known composition by weight. Cylinders were evacuated and subsequently filled with their identifying gas and nitrogen, with final pressure summing to 1785 psi. Cylinders were weighed after each component gas fill to ensure accurate ratios. Each cylinder was connected to the pressure cell, maintained at a constant temperature of 4.0° C, and subsequently released, pressurizing the cell to the full potential. Pressure was then released incrementally by 100 psi units and a Raman spectrum was taken with each decrease.

Peak area ratios were divided by R values to generate relative ratios, which were then used to calculate composition percentages of the cylinder gas space:

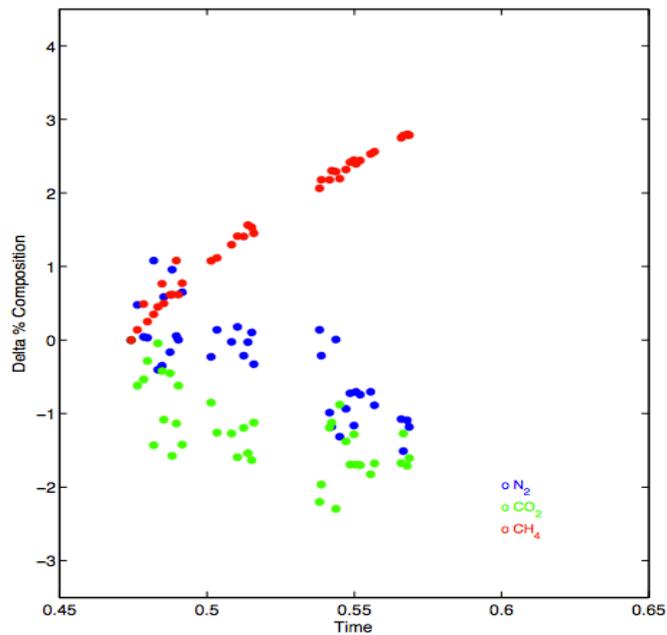
$$\text{Moltotal}/\text{N}_2 = [\text{CO}_2/\text{N}_2]/R + 1 + [\text{CH}_4/\text{N}_2]/R$$

$$\text{N}_2 \% = 100(\text{Moltotal})^{-1}$$

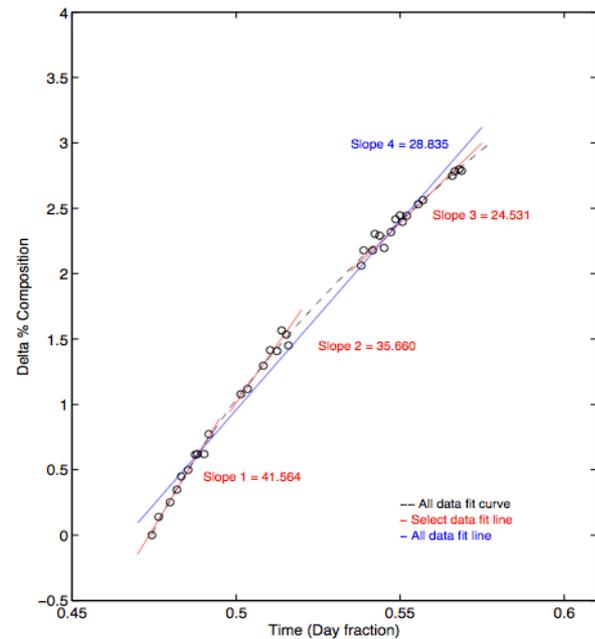
$$\text{CO}_2 \% = 100 [\text{CO}_2/\text{N}_2]/R$$

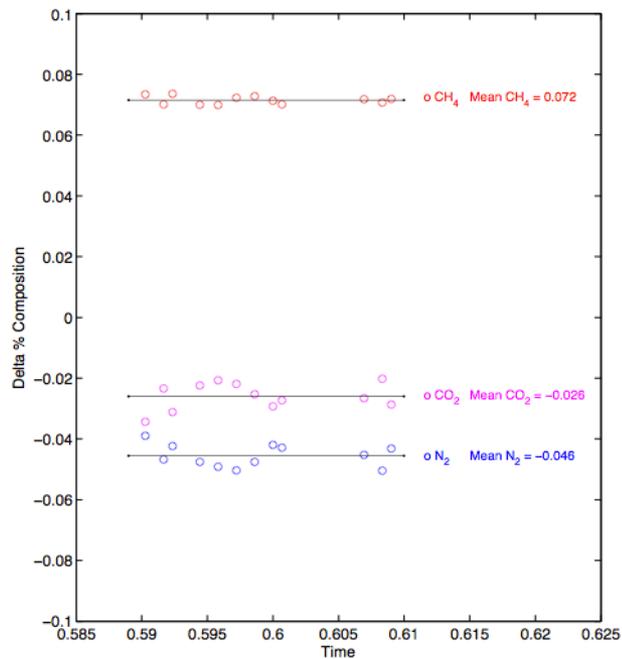
$$\text{CH}_4 \% = 100 [\text{CH}_4/\text{N}_2]/R$$

Analyzing the gas phase data: Rapid increase in CH₄, declines in CO₂ and N₂



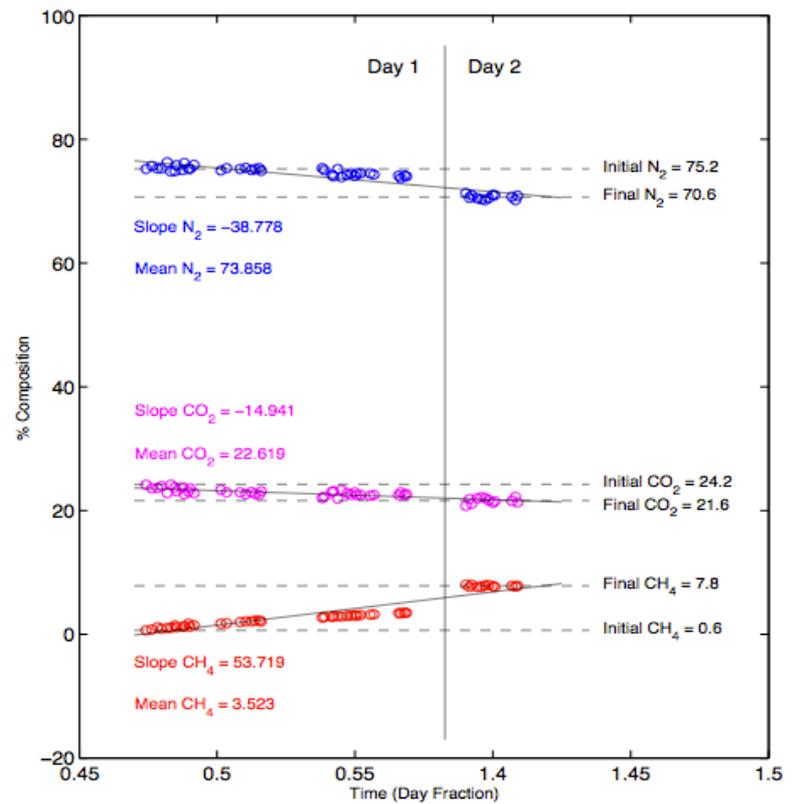
Change in % composition over 2 hours





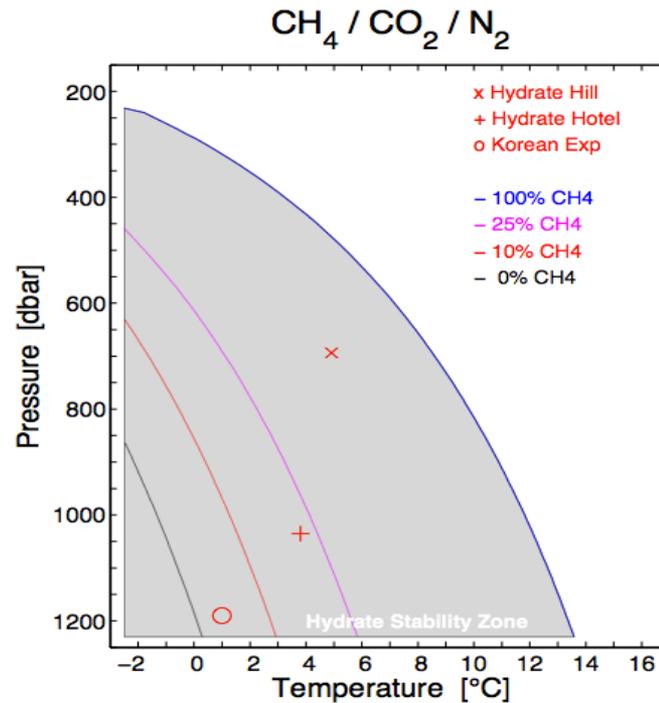
Change in gas composition Day 2

**Combined change in gas composition:
Day 1 and 2**



What does the phase diagram tell us?

A CH₄-N₂-CO₂ gas mixture will form a hydrate. Under the pressure cell conditions of Park et al. (2006) this will occur with 5-10% CH₄; only 10-15% lower than in our field test. It appears very difficult to form a pure CO₂ hydrate under these conditions. And hard to produce CH₄ gas.



The hydrate formation boundary space

Lessons Learned:

Things went quickly! The visual evidence clearly showed not “swapping” of guest molecules but simple sublimation of the solid methane hydrate into lower chemical potential gas phase. This was accompanied by the release of water as the hydrate dissociated into its basic components – no longer held together by the van der Waals force of the encaged gas.

The solubility of CO₂ in water is ~10x that of CH₄, and the CO₂ gas introduced did not form a hydrate but did dissolve in the liberated water phase, and since this solution is more dense than pure water it flowed down the face of the hydrate “stick” providing a fresh hydrate face for continued breakdown and gas release.

The thermodynamic end point was not reached here since we ran out of solid hydrate quickly. But realistic calculations show that in a contained system an equilibrium point will be reached at which further hydrate dissociation does not occur and equality of chemical potential is reached.

The big picture - A multi-million \$ project:

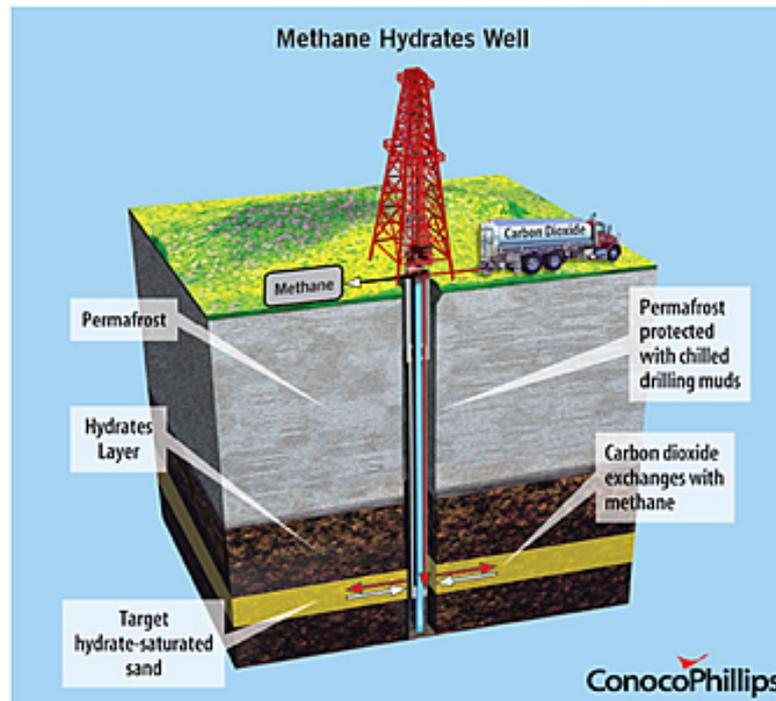
In 2002, DOE initiated a project with BP that has been conducted in collaboration with the U.S. Geological Survey. The project used existing seismic and well data to define 14 drilling prospects in the Milne Point area that were projected to contain 600 billion cubic feet of gas in place. In early 2007 the project successfully drilled, cored and tested the Mt Elbert well. The well provided 100 feet of hydrate-bearing core with hydrate saturations as high as 75% of pore volume in predicted zones. A Modular Formation Dynamics test provided key information on the manner in which hydrates reservoirs responded to depressurization. Data and analysis related to the Mt. Elbert well program were published in the [February 2011 volume of the Journal of Marine and Petroleum Geology](#). Additional reports and publications about the project and well are available at the [NETL website](#).



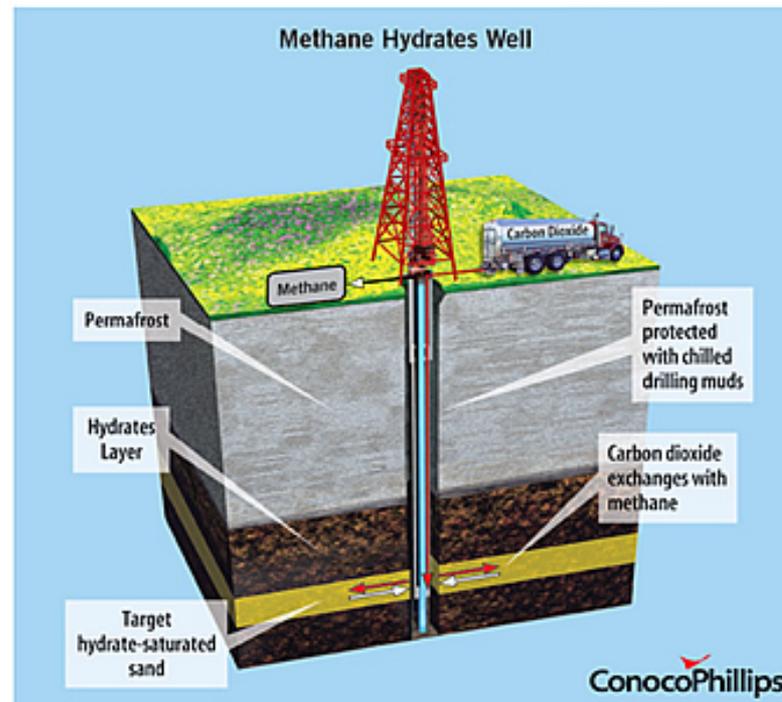
A large scale experiment on the Alaskan North Slope

DOE-ConocoPhillips Project

In 2008, DOE initiated a [project with ConocoPhillips](#) to test CO₂ injection as a mechanism to produce methane from hydrate in Prudhoe Bay. Laboratory experiments have shown that injected CO₂ will replace the methane in the hydrate structure, releasing the methane for production. This technology would have added benefits in storing CO₂ in the subsurface and preventing surface subsidence by maintaining the integrity of hydrate-cemented formations. A two-year project is planned. The Ignik Sikumi #1 well was drilled, tested and temporarily abandoned using an ice pad adjacent to Prudhoe Bay Unit L-pad in March and early April 2011. The Department of Energy has partnered with ConocoPhillips and the Japan Oil, Gas and Metals National Corporation to conduct a test of natural gas extraction from methane hydrate using a unique production technology, developed through laboratory collaboration between the University of Bergen, Norway, and ConocoPhillips, for the 2012 Ignik Sikumi Gas Hydrate Field Test. This ongoing, proof-of-concept test commenced on February 15, 2012, and concluded on April 10. The team injected a mixture of carbon dioxide (CO₂) and nitrogen into the formation, and demonstrated that this mixture could promote the production of natural gas. Ongoing analyses of the extensive datasets acquired at the field site will be needed to determine the efficiency of simultaneous CO₂ storage in the reservoirs.



Analysis: It appears likely that the injection of a N₂-CO₂ gas mixture into the formation displaced CH₄ saturated water and put the hydrate bearing sands into direct contact with the gas phase. Sublimation of CH₄ into the CH₄ poor, N₂-CO₂ rich, gas phase. This was seen as released gas. It is likely that the injected CO₂ began to dissolve both into the produced water from hydrates and into the original formation waters that were displaced. Quite quickly the system would evolve into a CH₄-N₂ gas mixture depleted in CO₂. This would form it's own hydrate phase and the reaction would stop.



Some more details from Ko-ichi:

The gas production test was closed around 14 (2PM) on March 12 in Japanese standard time. It was due to:

1. The trouble of hydraulic pump for depressurizing the well happened from early morning of the 12th.
2. The increasing sand excretion to the production well was observed and they confirmed that the production of gas was not normal as they expected.
3. The severe weather decline was forecasted in the area.
4. Some sign of hydrate dissociation was observed at the monitoring well about 20-m apart from the production test well.

Production period: about six days

Accumulated gas production: about 120,000 cubic meters
Mean daily gas production: about 20,000 cubic meters

NOTE: All values are tentative. They would be updated later.

In the same report they referred the 2008 Malik test results as:

Production period: 5.5 days
Accumulated gas production: 13,000 cubic meters
Mean daily gas production: 2,400 cubic meters

NOTE: The fluctuation of daily production was 2,000 to 4,000 cubic meters

Acknowledgments:



- Thanks to the fine team of crew, pilots, and scientists aboard the RV Western Flyer
- Thanks to the David & Lucile Packard Foundation for their support of MBARI
- No Federal Funds were awarded for support of this project

Some of the team: And for the CO₂-N₂ conversion credit goes to our fine USGS colleagues Steve Kirby, Laura Stern, and John Pinkston who fabricated the hydrate and created the pressure vessel used for containment and deployment. A real team effort.