



The Exchange Reaction Between Methane Hydrate and Carbon Dioxide: An Oceanic Feasibility Test

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Objective

To conduct a feasibility test on the exchange reaction between a naturally occurring methane (CH₄) hydrate and liquid carbon dioxide (CO₂) in the ocean. Specifically to assess:

(1) whether it is possible to conduct and monitor such an experiment *in-situ* using current technology and skills

(2) whether reasonable results could be obtained with a comparatively large scale - small surface area reaction system

1. Introduction

Large amounts of CH₄ in the form of solid hydrates are stored on continental margins and in permafrost regions. If the conversion of CH₄ hydrate to CO₂ hydrate could be achieved by simply bathing the CH₄ hydrate mass in liquid CO₂, these natural hydrate reserves offer the potential double benefit of sequestering captured fossil fuel CO₂ with recovery of liberated CH₄ gas as an additional energy source. This possibility has raised significant international interest, and several recent laboratory studies have explored the exchange reaction between CH₄ hydrate and CO₂ (see [section 2](#)).

Here we report results from the first *in-situ* oceanic experiment on this reaction, carried out as an experiment of opportunity during an expeditionary geochemical survey of the massive thermogenic hydrate mounds in Barkley Canyon (see [section 3](#)). The experiment was performed as a feasibility test (see [section 4](#)) to explore experimental procedure and to determine whether reasonable results (measurable exchange) could be obtained with a relatively large scale-small surface area system.

2. Previous studies

Komai et al. (2002) used Raman spectroscopy to observe the reaction between structure I (sI) CH₄ hydrate and gaseous CO₂ in a small pressure cell. They observed slow conversion rates (several hours), where CO₂ hydrate formed both at the surface and within the interior of the CH₄ hydrate samples, and water ice crystals were also produced. In a following study, Yoon et al. (2004) reported that surface shielding by CO₂ hydrate formed in the outer layers of the sample plays a key role in retarding the dissociation of CH₄ hydrate in the interior.

Lee et al. (2003) carried out a similar reaction using finely ground sI CH₄ hydrates to increase the surface area available for reaction, and ¹³C NMR to investigate details of cage occupancy. They observed that CO₂ replaces CH₄ in the large cages of the sI hydrate structure, where replacement was complete in less than 5 hours with a maximum recovery of ~64% of the CH₄ present in the initial hydrate. In an extension to this work, Park et al. (2006) reported an increased CH₄ yield of ~85% when a binary CO₂-N₂ gas mixture was used as the reactant, since N₂ could replace CH₄ present in the small cages of the sI hydrate structure.

Park et al. (2006) also presented results from the first experiment using a structure II (sII) CH₄ + C₂H₆ hydrate and CO₂ in both the gas (274.15K, 35 bar) and liquid (274.15 K, 42 bar) phases. They reported near identical results for the exchange reaction with CO₂ gas (recovery: 92% CH₄ & 99% C₂H₆) versus CO₂ liquid (recovery: 90% CH₄ & 97% C₂H₆). Interestingly, CO₂ was found to replace CH₄ in both the sII-large and sII-small cages where this replacement induced a continuous structural change to sI hydrate as the reaction proceeded and the critical guest composition limit for sII hydrate was exceeded.

In a novel study, Graue et al. (2006) provide the first example of liquid CO₂ displacement of CH₄ from sI hydrate resident within a porous sandstone (277.15K, 81.6 bar) using 3D MRI to monitor the exchange process over time. These authors report initially rapid CH₄ production rates that decrease with time, where CH₄ production continued over 4 days, and flushing of the hydrate/sandstone plug with additional liquid CO₂ resulted in further CH₄ liberation.

All of the above experiments are laboratory studies; so far as we are aware we report results from the first attempt at a field experiment on the exchange reaction between a naturally occurring complex gas hydrate and liquid CO₂.

3. Study Area

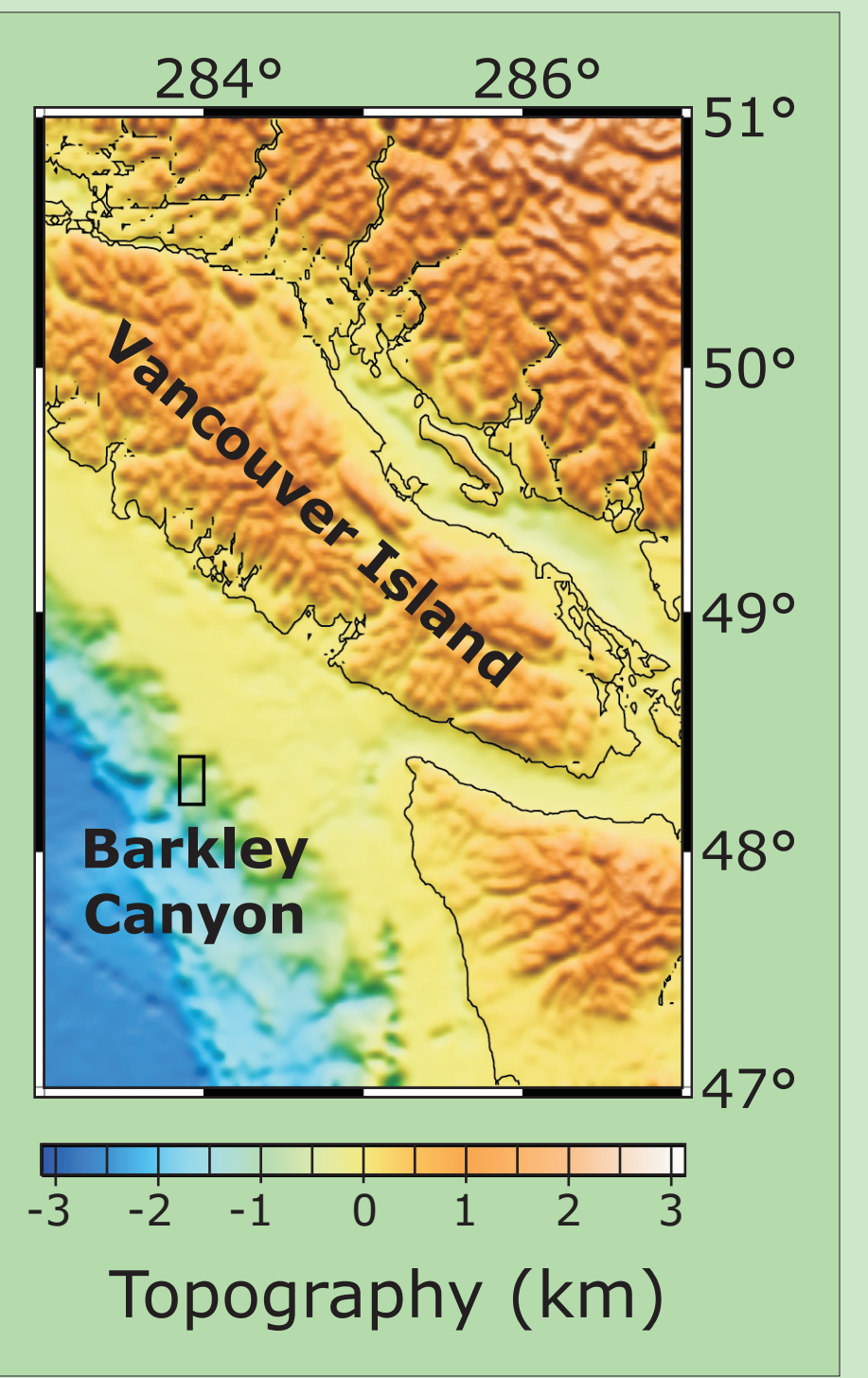
The feasibility test was carried out in August 2006 during a survey of the massive thermogenic hydrate mounds that outcrop from the seafloor at water depths of 850 m in Barkley Canyon, offshore from Vancouver Island (48°18.642' N, 126°3.903' W).

The Barkley Canyon hydrates have been surveyed and discussed previously by Pohlman et al. (2005) and Lu et al. (in press). The results of our recent survey are reported in companion papers in this session:

Details of hydrate composition and structure based on *in-situ* Raman spectroscopy and laboratory analysis of recovered samples are presented by Hester et al. in poster [MR43A-1071](#).

Further information on hydrate composition and the experimentally determined *in-situ* hydrate dissolution rates are presented by Peltzer et al. in poster [MR43A-1067](#).

Finally, a detailed multibeam bathymetry, subbottom and sidescan survey of the site is presented by Caress et al. in poster [MR43A-1063](#).



4. The Feasibility Test

The Challenge

conducting and monitoring an exchange reaction between naturally occurring CH₄ hydrate and liquid CO₂ in the ocean presents a number of difficult challenges, not least of which are:

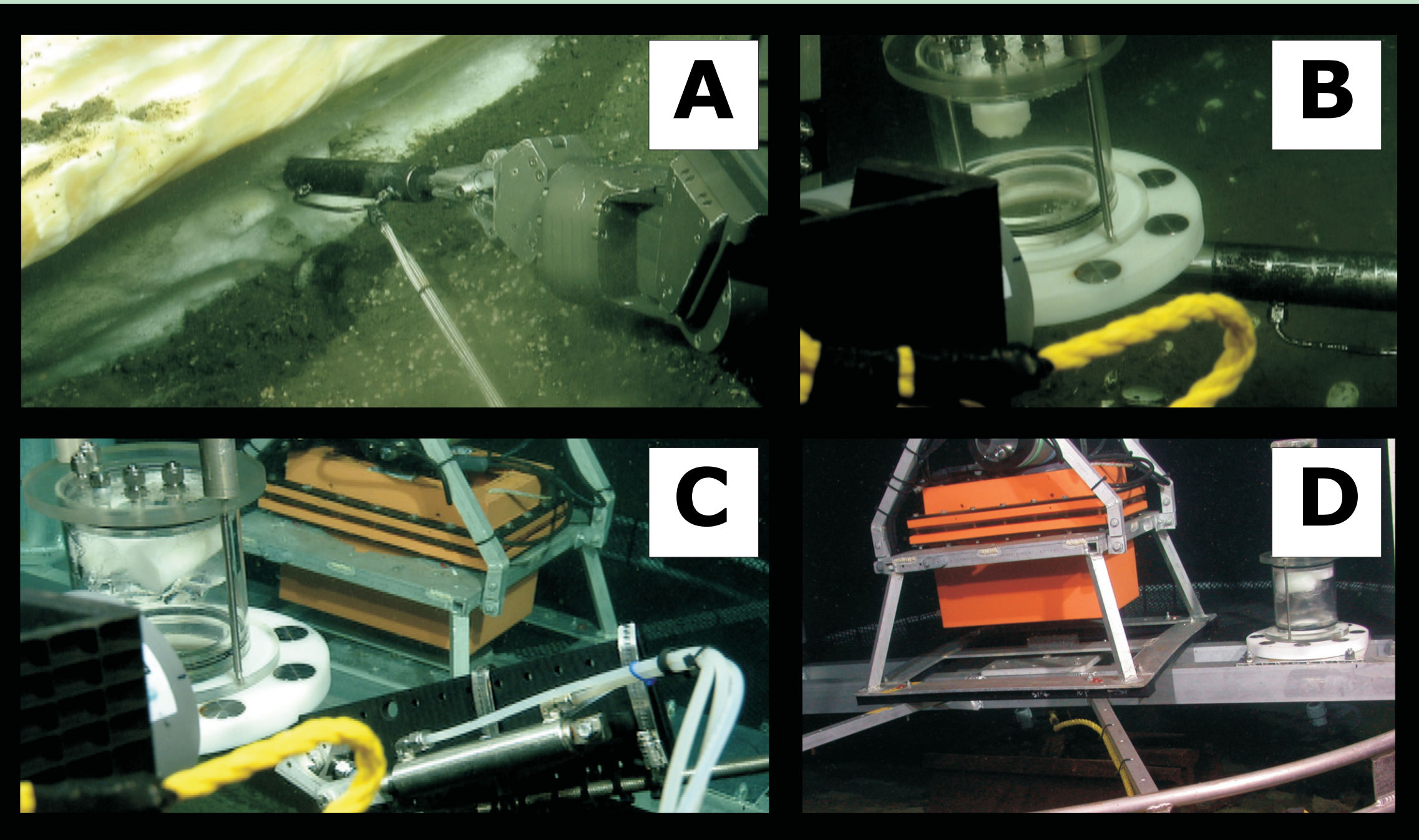
- Methodological and analytical techniques used routinely in the laboratory are generally not available for use in the deep-ocean. Furthermore, natural hydrate samples, and the surrounding sediments, can be strongly fluorescent, thus posing challenges for optical techniques.
- The hydrate composition and structure are defined by the sample. While laboratory studies have focused on simple synthetic sI CH₄ hydrates or sII CH₄ + C₂H₆ hydrates, naturally occurring hydrates are more complex and may exhibit significant heterogeneity in terms of guest gas composition and hydrate structure.
- The physical properties of the experiment cannot be controlled. The P-T field is set by the external environment, and the hydrate surface area available for reaction is dependent on the naturally occurring hydrate fabric.

In earlier work we have developed techniques for safely containing, transporting and dispensing liquid CO₂ in the deep-sea (Brewer et al., 1999). We have also developed the sea-going laser Raman spectrometer DORISS (Deep Ocean Raman In Situ Spectrometer, Brewer et al., 2004), which can be deployed in conjunction with PUP (Precision Underwater Positioner, White et al., 2005) to enable precise positioning of the laser focal point with sub-mm accuracy (see [Figure H section 6](#)). This system has been successfully employed to examine the composition and structure of naturally occurring gas hydrates at the seafloor (Hester et al., 2006).

Here we combine these tools and skills to conduct a simple short term oceanic field test on the CH₄-CO₂ hydrate exchange reaction. This feasibility study was conducted with a 'learning by doing' approach, where our principal objectives were to identify methodological problems and/or improvements for future experiments, and to determine if measurable exchange occurred between a macroscopic natural gas hydrate and liquid CO₂ under the P-T conditions at the sea-floor.

Methodology

The systems described below were deployed and controlled using the Remotely Operated Vehicle (ROV) Tiburon, where this work would not have been possible without the skills and dedication of the Tiburon pilots.



(A) Two small cores (10 cm length, 4 cm diameter) of the white hydrate were collected from exposed outcrops using an ROV operated tool. The release of some small gas bubbles was observed during coring.

(B) The cores were hydraulically ejected into a glass walled, closed top, reaction chamber. Note the well defined surface boundaries of the fresh cores. Raman spectra of the unreacted hydrate cores were obtained using DORISS II & PUP (see [section 6](#)).

(C) Approximately 2 L of liquid CO₂ were dispensed into the chamber. Under ambient conditions (P = 870 dbar, T = 4.0 °C, S = 34.2), the densities of the gas hydrate and liquid CO₂ were closely matched and less than that of seawater, where the hydrate cores floated at the top of the chamber fully immersed within the buoyant liquid CO₂.

(D) The chamber was then placed on an aluminium base plate to seal the system.

Over the following ~48 hours, the system was periodically inspected with the ROV HDTV camera (see [section 5](#)). At the end of the experiment the chamber was transferred to PUP for examination with DORISS II (see [section 6](#)).

5. Visual Observations on Addition of CO₂

The two panels opposite show the front and rear views of the reaction chamber over the 2 days of the experiment.

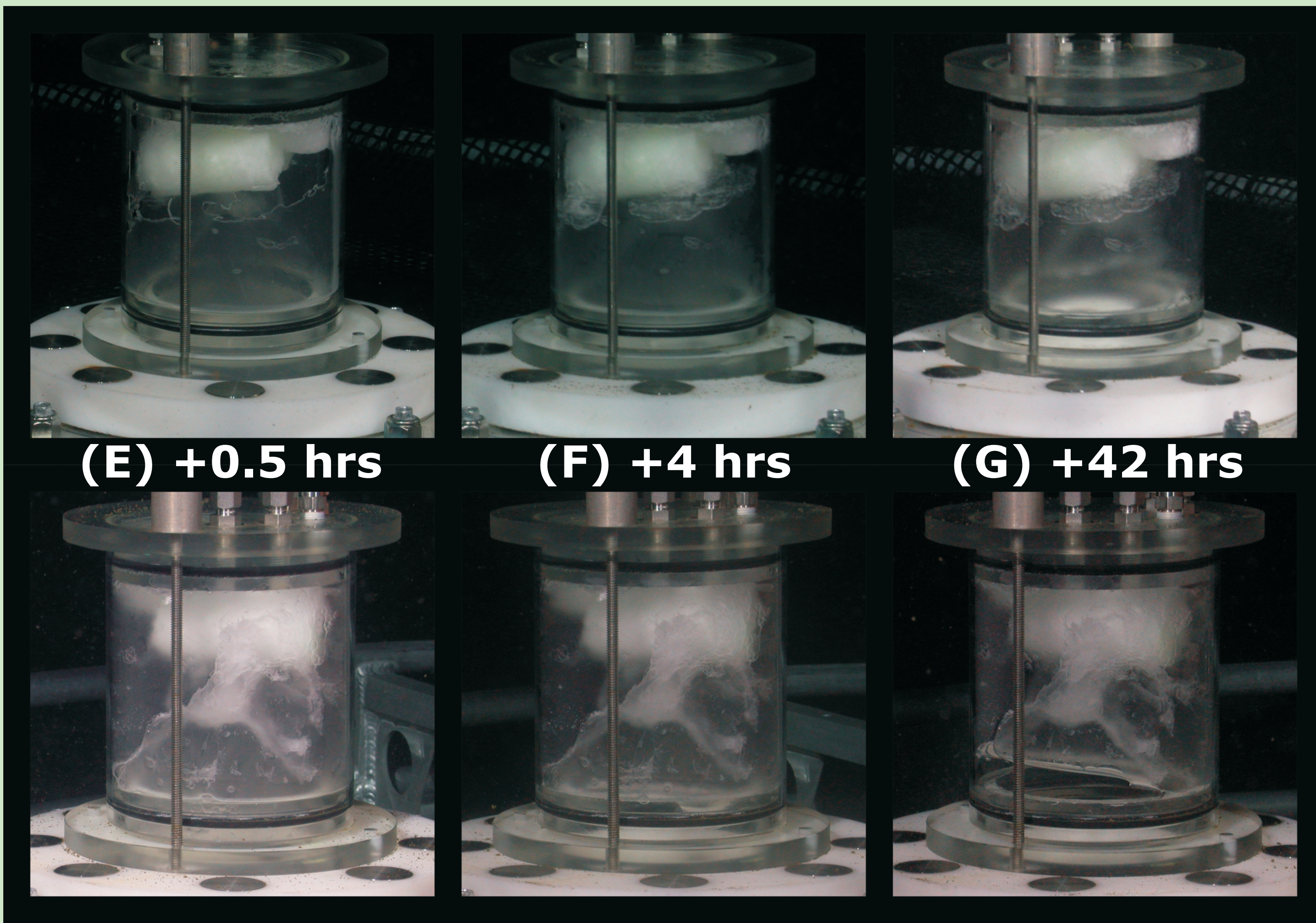
CO₂ Hydrate 'Frosting' & Membrane Formation

A 'frosted' CO₂ hydrate film can be seen on the inner wall of the reaction chamber, while the rear view shows additional CO₂ hydrate membrane formation within the vessel interior.

The formation of CO₂ hydrate membranes is an artefact of the liquid injection process, although the continued growth of the membranes over time may reflect an ongoing exchange process.

When liquid CO₂ is exposed to seawater under *in-situ* conditions, a hydrate membrane forms at the interface almost instantaneously. The style of injection (with the dispensing nozzle held beneath the reaction chamber - see [Figure C](#)), exacerbated this effect due to the turbulent injection of numerous CO₂ droplets.

In future work care must be taken to avoid the formation of CO₂ hydrate during the injection process. This can be achieved by the slow injection of liquid CO₂ through a port on the chamber top, thereby avoiding turbulence, limiting the surface area of the seawater-CO₂ interface, and effectively displacing droplets from the chamber walls so that a frost-free surface is achieved (Dunk et al., 2005).



Core 'Fluffiness' & Gas Bubbles - Evidence for Replacement?

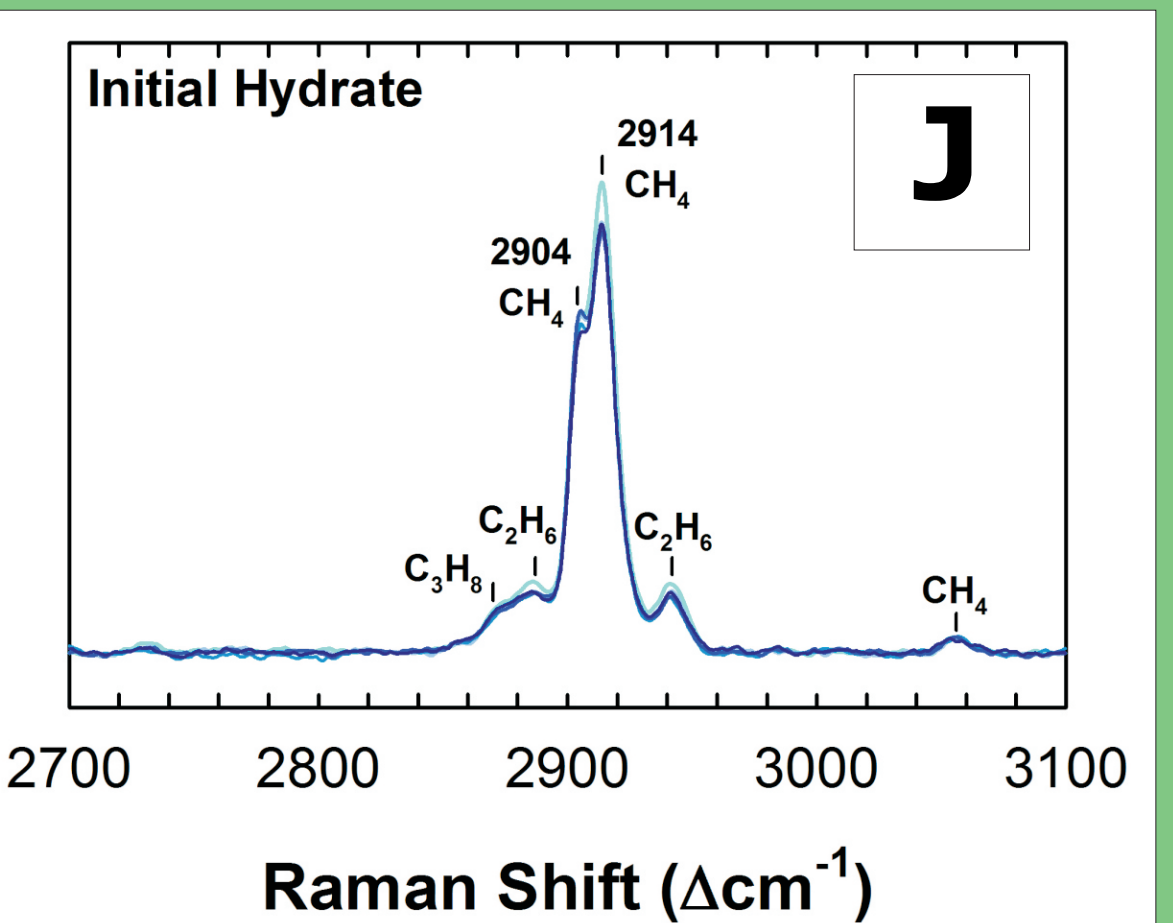
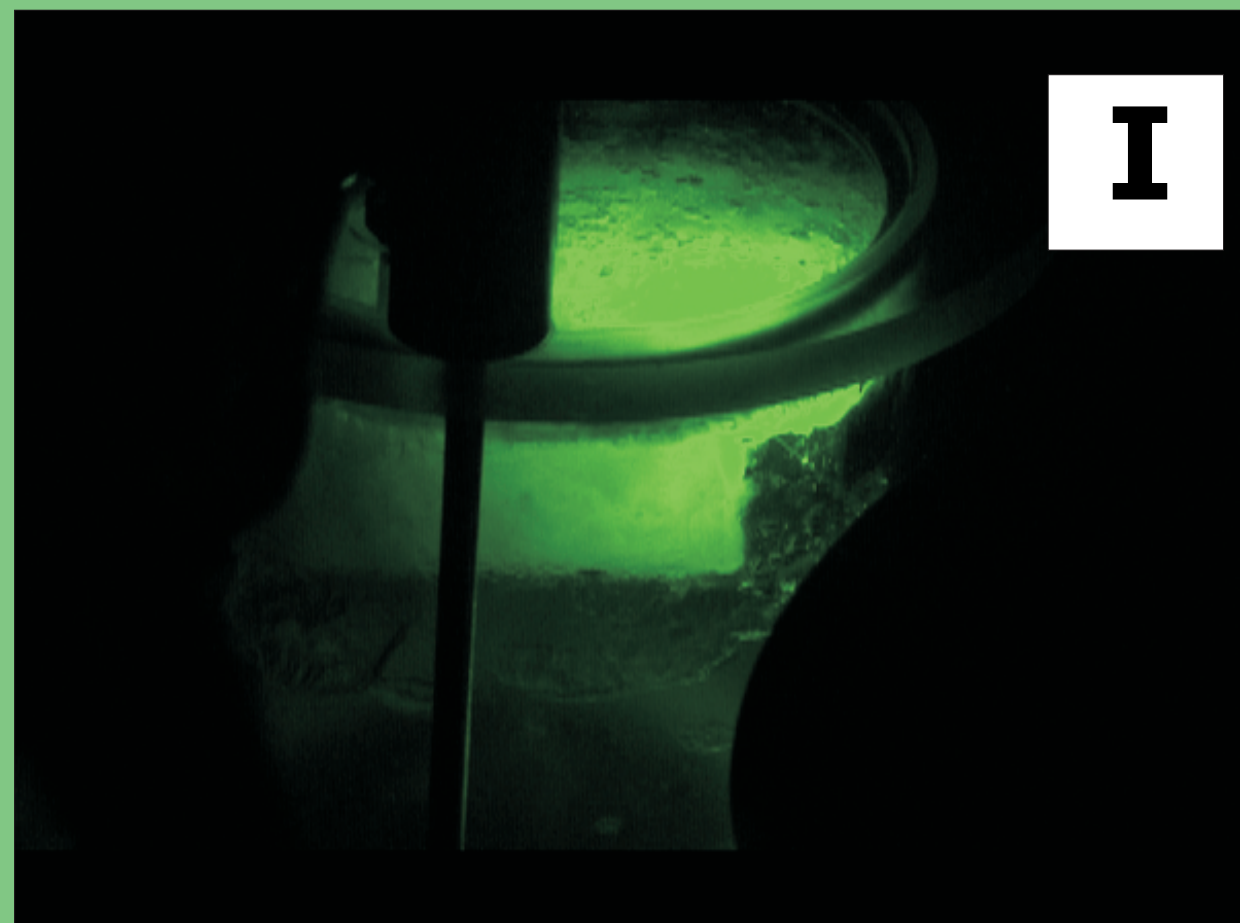
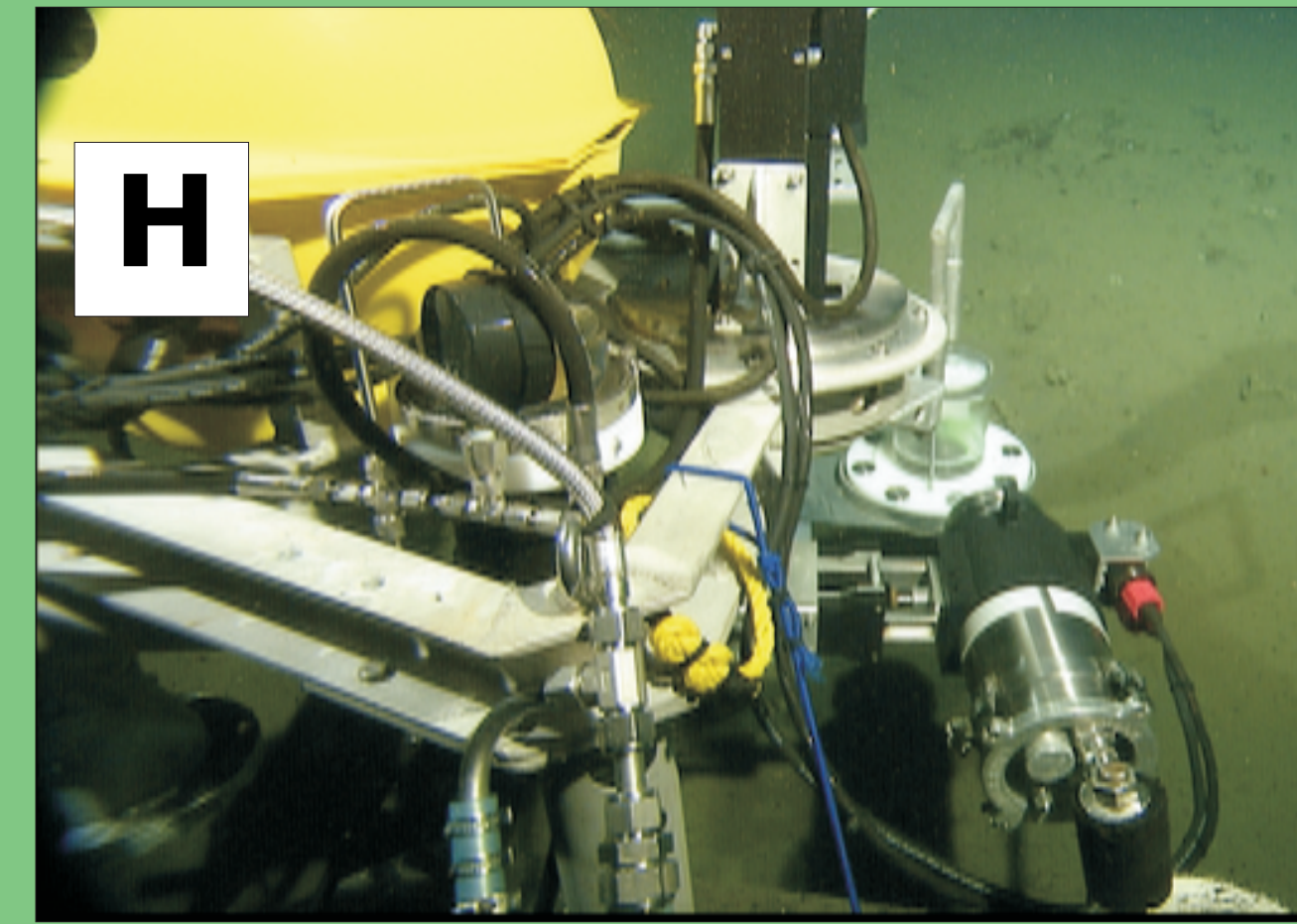
At the start of the experiment, the boundaries of the hydrate cores were sharply defined ([Figure B & C in section 4](#)). 30 minutes later, the hydrate core boundaries had taken on a 'fluffy' appearance ([Figure E](#)), where the 'fluffiness' increased over the remainder of the experiment ([Figures F & G](#)). That the core boundaries were well defined immediately following addition of CO₂ ([Figure C](#)) implies that the 'fluffy' factor is not due to an experimental artefact (i.e. it is unlikely that the fluffiness results from the formation of a CO₂ hydrate membrane without any interaction with the hydrate core). We therefore suggest that the increase in 'fluffiness' reflects an ongoing process occurring at the core boundary such as (i) exchange leading to restructuring of the hydrate and/or (ii) dissolution of the hydrate with regrowth of a secondary hydrate.

We also observed the formation of a small but visually identifiable bubble layer at the top of the chamber. While free gas was not detected in the Raman spectrum of the initial hydrate (see [Section 6](#)), we note that this gas may have been originally present and thus not originate from a true displacement reaction.

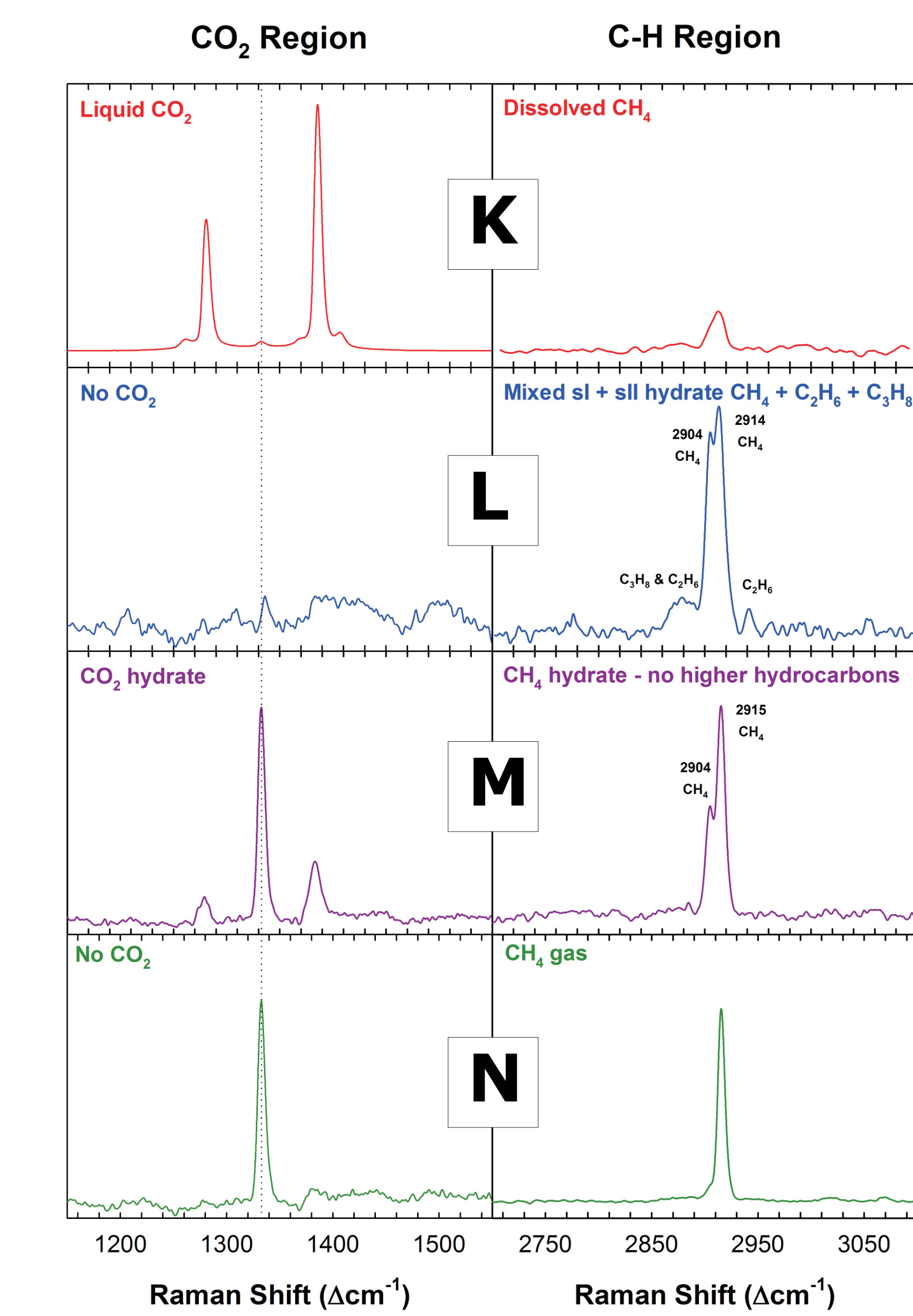
6. Raman Spectroscopy

In-situ Raman analysis was performed on the hydrate cores prior to injection of liquid CO₂, and approximately 48 hours following injection of liquid CO₂. Note all Raman spectra shown below have been baseline corrected to remove interference fluorescence and the water stretching bands.

For *in-situ* analysis the chamber was transferred to PUP which allowed precise positioning of the laser focal point ([Figure H](#)).

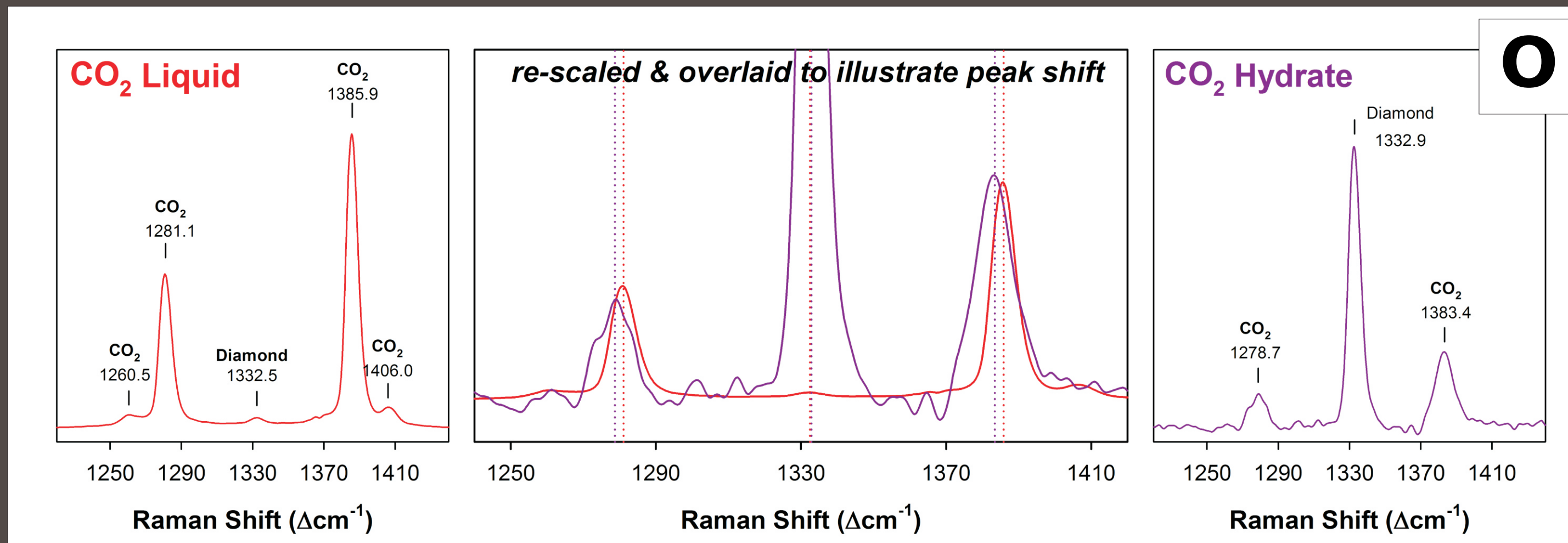


ROV lights were turned off during spectral acquisition ([Figure I](#)). 5 spectra were collected of the hydrate prior to injection of CO₂ ([Figure J](#)). The ratio of the 2904:2914 Δcm^{-1} CH₄ bands and the presence of higher hydrocarbons indicates a mixed sI and sII hydrate structure.



Liquid CO₂ shows the Fermi diad (1281 & 1386 Δcm^{-1}) with hot bands (1260 & 1406 Δcm^{-1}). On enclathration, the Fermi diad peaks broaden and red shift (1279 & 1383 Δcm^{-1}) and the hot bands can no longer be distinguished. Park et al. (2006) report a shift in the hydrate peaks from 1278 & 1386 Δcm^{-1} in sII to 1277 & 1382 Δcm^{-1} in sI. It is unclear from our data whether the CO₂ hydrate is in the sI or sII structure, or a mixture of the two. This is an area for future investigation and requires calibration of the spectrometer under *in-situ* conditions by measuring CO₂ in synthetic hydrates of known composition to determine whether the structures can be resolved.

Focusing on CO₂ in the liquid & hydrate phases



The initial success of this pilot study bodes well for future investigations of the oceanic exchange reaction between CO₂ and natural gas hydrates

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