In Situ Raman Spectroscopic Measurements of Undisturbed Seafloor Clathrate Hydrate at Barkley Canyon

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1. Objective

To determine the properties, such as the structure and composition, of naturally occurring gas hydrates in situ using laser Raman spectroscopy. To recovery hydrate samples for laboratory measurements using Raman, NMR spectroscopy, and X-ray diffraction.

2. DORISS Sea-Going Raman Spectrometer

DORISS II (Deep Ocean Raman *In Situ* Spectrometer) is a seagoing Raman spectrometer that has been deployed on remotely operated vehicles (ROV) (Brewer et al., 2004; Pasteris et al., 2004).

The spectrometer and on-board computer for communications and control were packaged in two pressure housings rated to 4000 m depth. The optical probe head is contained in titanium housing with a dome glass window. The probe was positioned using the Precision Underwater Positioner.

The Precision Underwater Positioner (PUP) was employed along with the Raman probe to provide the ability to analyze solid, opaque samples subsea (White et al., 2005)

DORISS II (On bench)

PUP

Controlled by a ship-board scientist, PUP is capable of moving the probe head with a precision of 0.1 mm in three dimensions – two linear and one rotational. The focus stage inside the probe head provides an additional dimension of movement.

3. Other Instrumentation

Hydrate Corer

The Hydrate Corer was made from stainless steel. The ROV arm rotated the corer into the hydrate. A hydraulic actuator was used to release the hydrate from the corer

The clathrate bucket allows for pressurized recovery of hydrate samples. A plexi-glass cover acted as a temperature buffer during the recovery through the water column. On deck, the pressure was released and the hydrate sample was quenched in liquid nitrogen.

Clathrate Bucket

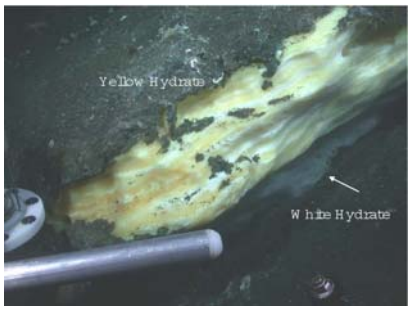
4. Geological Setting

Barkley Canyon on the Cascadia Margin is an area known for it vast quantities of seafloor hydrates at 850-860m depth (Pohlman et al., 2005; Chapman et al, 2004.)

This site provided an ideal study area due to the large quantities of hydrates that exist exposed as pure hydrate fractions.

A light-weight oil stained much of the yellow hydrate.

5. Two Hydrate Fabrics Observed at One Site

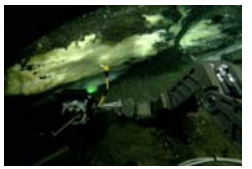


Two hydrates fabrics were found in close proximity. The yellow hydrate was oil-stained with bands of various degrees of coloration from the oil. This "hard" yellow hydrate was resistant to coring.

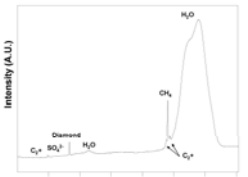
The white hydrate appeared to have little to no oil staining. The "soft" white hydrate was cored much more easily versus the yellow hydrate. Small gas bubbles could be observed while coring the white hydrate.

6. In Situ Hydrate Measurements at Barkley Canyon

The DORISS probe head was presented to deep sea hydrate targets with either PUP or the ROV manipulator (shown right). Once close, the laser was precisely focused until optimal Raman spectra were achieved. Raman spectra were processed in real time via a laptop computer.

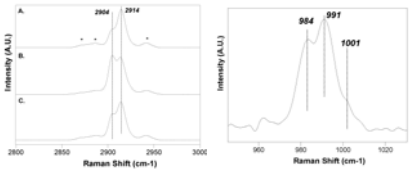


7. In Situ/Laboratory Measurements-White Hydrate

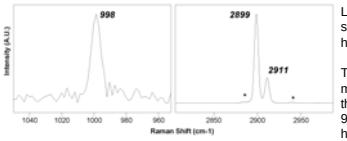


In situ Raman spectrum of white hydrate fabric. Along with Raman peaks for methane, higher hydrocarbons such as ethane, propane, and butanes were observed.

Unlike in situ measurements at Hydrate Ridge, no free gas was detected when measuring the hydrate (Hester et al., Submitted).



In situ Raman spectra of "white" hydrate samples. Variability in CH_4 peak intensities at 2904 and 2914 cm^{-1} was observed. The change in the CH_4 peak ratio is due to the co-existence of sI and sII hydrate. The ethane peak at 991 cm^{-1} is for sII hydrate, while 1001 cm^{-1} is for sI hydrate.

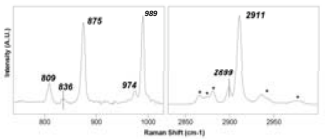


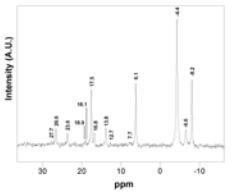
Laboratory Raman spectrum of "white" hydrate sample.

The ratio of the methane peaks and the ethane peak at 998 cm^{-1} indicated sI hydrate.

Laboratory Raman spectrum of "white" hydrate sample on a different location.

The hydrate was determined to be sII from the ethane, propane, and butane peaks.





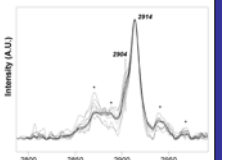
Laboratory NMR spectrum of "white" hydrate sample. While Raman measures a small area, the NMR detects a bulk sample.

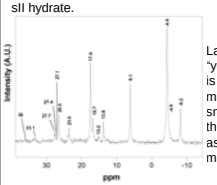
The hydrate is a mixture of sI and sII. The peak at -6.6 indicates methane in the large cage of sI; -8.2 is the large cage of sII. Peaks for ethane, propane, and butane are also present.

8. In Situ/Laboratory Measurements-Yellow Hydrate

In situ Raman spectrum of yellow hydrate fabric. Because of fluorescence, only the C-H peaks were detectable.

Multiple measurements were made on the hydrate specimen at different locations. All were quite similar and they indicated sII hydrate.

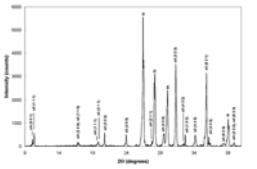




Laboratory NMR spectrum of "yellow" hydrate sample. The hydrate is a mixture of sII and sH. The methane peaks are for sII and a small shoulder at -4.9 for methane in the medium cage of sH. Peaks are assigned to sH formers such as methylcyclohexane.

Laboratory X-ray diffraction pattern of "yellow" hydrate sample.

The hydrate was a mixture of mainly sII (a = 17.180 Å), with small reflections for sH hydrate (a = 12.237 Å, c = 10.091 Å).



9. Conclusions

- ❖ Hydrate samples measured in situ with Raman spectroscopy
  - At Barkley Canyon on the Cascadia margin
- ❖ Two types of hydrate fabrics observed
  - White "soft" hydrate
    - Heterogeneous mixture of sI and sII
  - Yellow "hard" hydrate
    - Mainly sII with sH detected
  - No free gas was present in the in situ hydrate spectra
    - Different for the seafloor hydrates at Hydrate Ridge
- ❖ Recovered hydrate samples measured in laboratory
  - Using Raman, NMR spectroscopy, and X-ray diffraction
  - Laboratory and in situ measurements were complimentary

10. References

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11. Acknowledgements

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