First Expeditionary Deployments of the Deep Ocean Raman In Situ Spectrometer

S. N. White (sheri@mbari.org), P. G. Brewer (brpe@mbari.org), E. T. Peltzer, W. Kirkwood Monterey Bay Aquarium Research Institute, Moss Landing, CA 95039
J. D. Pasteris Washington University, Dept. of Earth & Planetary Science, St. Louis, MO 63130
N. Nakayama Hokkaido University, Div. of Earth and Planetary Science, Sapporo, Hokkaido 0600810, Japan

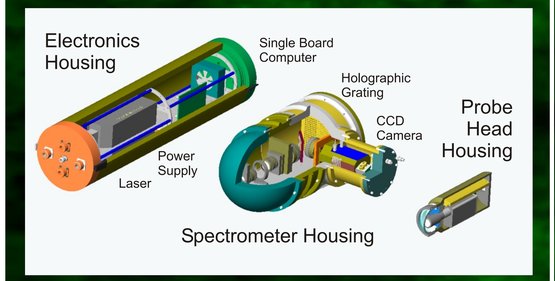
OS32A
0235

ABSTRACT

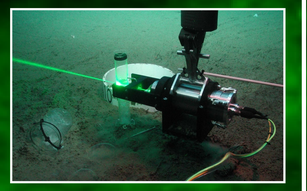
MBARI's *in situ* laser Raman spectrometer (DORISS Deep Ocean Raman In Situ Spectrometer) was deployed at gas vents in Guaymas Basin, Gulf of California in 2003. The first *in situ* Raman spectra of natural gas venting from the sea floor were obtained. These spectra will be compared to GC analyses of samples collected at the same vent and Raman analyses of pure methane deployed as a standard for at-sea testing.

Laser Raman spectroscopy is a powerful geochemical technique for analyzing the chemical composition and molecular structure of solids, liquids, and gases. The prototype deep-ocean Raman instrument is based on an off-the-shelf laboratory model from Kaiser Optical Systems, Inc. Engineering test deployments conducted over the past 1.5 years have proved that Raman spectra of high quality can be obtained in the deep ocean. We have acquired spectra from solid, liquid and gaseous standards deployed as deep as 3600 m in the ocean. We are currently in the next phase of development which consists of using DORISS for exploratory measurements of natural targets in the deep ocean.

During an expedition to the Gulf of California on the R/V Western Flyer in 2003, DORISS was deployed successfully by the ROV Tiburon at natural gas vents on the sea floor (~1700 m depth). The laser probe head was focused into a small volume of gas trapped in a sampling funnel. Spectra were collected of gas samples at the vent site and at depths above the hydrate stability zone. Bands for methane dominate the spectra. Attempts to collect spectra of natural gas hydrates at the vent were difficult due to the stringent positioning requirements of the probe head when analyzing solid, opaque targets. This problem has been addressed by the development of a precision underwater positioner that provides a stable platform for analyses and movement of the DORISS probe head with a precision of 0.1 mm.



The DORISS instrument is divided into three pressure housings (above). The Electronics Housing holds the laser, power supply, and single-board computer. The Spectrometer Housing contains the spectrometer, CCD and associated electronics. These two housing are mounted in the ROV toolsled. The Probe Head housing contains the optical head and is deployed to the target via ROV manipulator (right).



DORISS Instrument

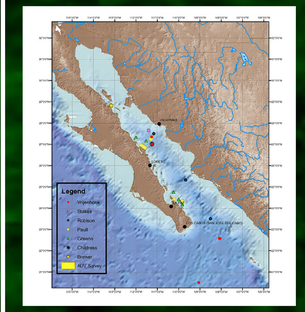
DORISS (Deep Ocean Raman In Situ Spectrometer) is based on a laboratory model laser Raman spectrometer from Kaiser Optical Systems, Inc. It consists of a 532 nm Nd:YAG laser, a holgraphic transmissive duplex grating, a 2048 x 512 front-illuminated CCD camera from Andor Technology, and a holographically filtered optical head with interchangeable sampling optics. The grating covers the 100-4400 cm^{-1} spectral region and splits the spectrum into two stripes on the face of the CCD, providing a mapping of ~1 cm^{-1} per pixel.

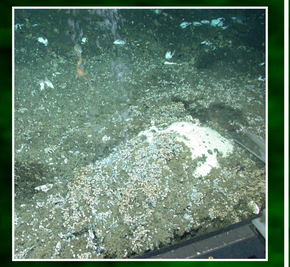
The two sampling optics used were a stand-off optic and an immersion probe. The stand-off optic is used behind a dome window and has a working distance of 0-10 cm from the dome to the target. Its focal depth is ~3 mm in water. The immersion probe consists of a 2 mm focal distance lens at the end of 10 inch long, 0.5 inch diameter metal tube with a plane sapphire end window. The working distance is water is 1-7 mm from the probe tip and the focal depth is ~1 mm in water. When using the immersion optic, the dome window of the probe head housing is replaced with a flat titanium endcap with a gland seal (picture at right). The stand-off optic, with its larger depth of focus provides greater flexibility, but with lower power density. The immersion optic with its higher power density is preferred when analyzing gases, but its small depth of focus requires precision positioning when used on opaque targets. Both optics were used during the expedition described here.

The DORISS instrument was calibrated every time the sampling optics were changed. The calibration kit provided by Kaiser includes a neon source for wavelength calibration, a tungsten source for intensity calibration, and a cyclohexane standard for laser wavelength calibration. A diamond plate was installed in the laser path within the probe head but off focus. The strong, stable 1332 cm^{-1} line is superimposed on all spectra providing a calibration reference during deployment.

Instrument details can be found in Brewer et al., submitted.

Gulf of California Expedition

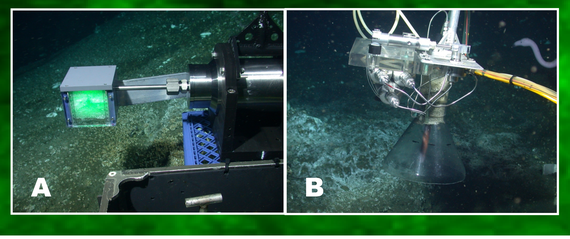




The preferred method of obtaining gas spectra was though use of the immersion optic protruding into an open-bottomed cube (picture A below). Gas was trapped in the cube forming a gas space around the immersion optic (i.e., no seawater was present in the beam path). Both configurations were successful for analyzing gas samples. The one problem was the formation of a partially-opaque hydrate skin on the window of the immersion probe and the glass top of the sampling funnel. This partially blocked both the exiting beam and the backscattered signal, thus greatly reducing the sensitivity. Once the sample was brought above the hydrate stability zone (~400 m depth) clean, high quality spectra could be obtained.

Gas Samples

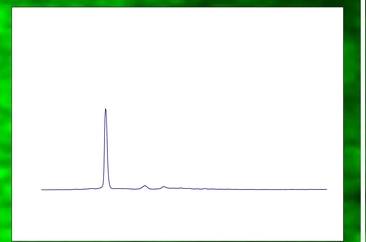
Gas samples for shore based analysis were collected in 150 ml stainless steel cylinders. Three evacuated cylinders were integrated into a sampling funnel with a heating element (picture B below). The funnel was placed over the gas vent to collect a sample. During sample collect gas hydrate formed in the sampling funnel which could clog the lines to the cylinders. Therefore the heater was used to heat the sample and melt the hydrate. The gas could then be pulled into an evacuated cylinder by activating a valve. Sixteen samples were collected in this manner. These samples include gas bubbly from the vent, gas bubbles from various heights above the vent, gas within the sediment, and melted hydrate from within the sediment.



Raman Analysis

Raman spectroscopy is capable of determining the composition of natural gas [Diller and Chang, 1980]. The primary constituent of the vent gas was assumed to be methane which has a strong Raman peak at ~2917 cm^{-1}, and smaller peaks at 1535, 3020, and 3070 cm^{-1}. Higher hydrocarbons were also assumed to be present in measurable quantities. Raman spectra were obtained of the vent gas at the sea floor (1582 m, ~3.0°C) and at various depths in the water column using both the immersion optic and the stand-off optic.

Data processing was performed with the GRAMS/AI spectral processing package from ThermoGalactic. The GRAMS peak fitting algorithm uses the Levenberg-Marquardt method. Peaks were fit with Gaussian and Lorentzian curves, the baseline function was calculated and subtracted, and peak positions, heights, widths and areas were calculated.



Conclusions & Future Work

DORISS successfully obtained *in situ* Raman spectra of natural gas emanating from a vent on the sea floor. As verified by shore-based GC analysis, the gas was composed primarily of methane (~97%). Trace constituents were not present in high enough concentrations to be detected by Raman analysis. Two significant lessons were learned from this expedition. 1) When analyzing gases within the hydrate stability zone, a heater can and should be used to remove hydrate skin formed during collection. This was successfully done for the gas sample collection and would have greatly improved the Raman data collected on the seafloor. 2) Precision position is necessary when collecting Raman spectra of opaque targets (such as solid hydrate, hydrate skin, or rocks). This requirement is dictated by the focal volume of the sampling optics. A new Precision Underwater Positioner (PUP) has been built for this purpose and is described in the following poster (OS32A-0236).

Raman spectroscopy is a powerful geochemical tool that can now be used to analyze targets in situ in the deep ocean. We plan to continue expeditionary deployments of the DORISS instrument in 2004 during an expedition to Hydrate Ridge and the Cleft Segment of the Juan de Fuca Ridge. At these location we will attempt to use Raman spectroscopy to analyze gas hydrates in situ (using the PUP positioner), and to analyze various targets in hydrothermal vent environments -- vent fluids, bacterial mates, sulfides, etc.

GC Analysis

Methods

Vent gases and hydrates samples were trapped in a heated sampling funnel and collected in ~150 ml stainless steel pressure-tight syringes (right) using ROV Tiburon. For the determination of C_1~C_6 and CO_2 concentrations, we used a Hewlett Packard® 5890 gas chromatograph equipped with a flame ionization detector (FID) and a thermal conductivity detector (TCD) with He as carrier gas. Gas samples were transferred to a calibrated volume loop (0.0952 ml at 20°C for C_1, C_2 and CO_2, 1.002 ml at 20°C for C_3~C_6) before being injected onto a separation Porapak-Q column. Calibration was performed using a Scotty IV calibration gas (HC-MIX #9). Precision for replicate analyses averaged was ± 0.3% and ± 2% for C_1~C_3 gas and CO_2, respectively.

Results

Methane is the major hydrocarbon component (96.66~98.77%) of the gas sampled. CO_2 is the 2.73~3.15% range except at T0578 (1.43%). All the Samples have NMHC (C_2~iso-C_6) trace molecular distribution. The ratios of C_1/C_2 (<10^3) suggest the contribution of small amounts of thermogenic gases in the sampled fluids. We can also see small change in the concentration of C_1 and CO_2 gases in the water column above the vent (T0563, T0573). That could be controlled by bubble dissolution and rise rate, diffusion, mixing with "background " seawater after the supply from sea floor.

Table 1. Molecular compositions of vent gases and hydrates from the sea floor in Guaymas Basin, Gulf of California.

Dive #	Cylinder	C_1 %	C_2 %	C_3 %	i-C_4 %	n-C_4 %	i-C_5 %	CO_2 %	Description
T0563	Red	96.66	0.25	0.042	0.013	0.001	0.003	2.95	Main gas vent @ 1m
	Blue	96.71	0.24	0.042	0.013	0.001	0.003	2.73	Main gas vent @ 5m
	Black	97.33	0.25	0.042	0.013	0.002	0.003	2.88	Main gas vent @ 0m
T0566	Red	98.03	0.25	0.041	0.013	0.002	0.003	2.91	Main gas vent @ 0m
	Blue	97.59	0.25	0.269	0.062	0.052	0.009	2.94	Main gas vent @ 0m
	Black	97.50	0.25	0.283	0.065	0.053	0.009	2.95	Duplicate of Blue
T0573	Red	97.37	0.27	0.078	0.017	0.002	0.004	3.15	Main gas vent @ 0m
	Blue	97.01	0.26	0.077	0.017	0.002	0.004	3.06	Main gas vent @ 2-3m
	Black	96.90	0.27	0.080	0.018	0.003	0.004	3.08	Main gas vent @ 8-10m
T0576	Red	98.06	0.25	0.083	0.019	0.003	0.004	2.81	Sediment gas bubbles
	Blue	98.06	0.26	0.078	0.017	0.003	0.004	3.11	LRS excavation vent
	Black	98.77	0.26	0.082	0.018	0.003	0.004	2.91	3rd sample from disturbed site
T0578	Red	98.44	0.26	0.077	0.016	0.002	0.004	3.04	Small vent / same as LRS
	Blue	97.82	0.26	0.077	0.017	0.002	0.004	3.09	Main gas vent
	Black	98.36	0.26	0.077	0.017	0.003	0.004	3.03	Duplicate of Blue
T0578	Red	98.16	0.17	0.118	0.027	0.006	0.008	1.43	Sediment gas + clathrate

References

Brewer, P.G., G.E. Malby, J.D. Pasteris, S.N. White, E.T. Peltzer, B. Wopenka, J. Freeman, and M.O. Brown, Development of a laser Raman spectrometer for deep-ocean science, Deep-Sea Res., Submitted.
Brunsgaard Hansen, S., R.W. Berg, and E.H. Stenby, How to determine the pressure of a methane-containing gas mixture by means of two weak Raman bands, 3 and 2 2, J. Raman Spectrosc., 33, 160-164, 2002.
Diller, D.E., and R.F. Chang, Composition of mixtures of natural gas components determined by Raman spectroscopy. Appl. Spectrosc., 34 (4), 411-414, 1980.
Merewether, R., M.S. Olsson, and P. Lonsdale, Acoustically detected hydrocarbon plumes rising from 2-km depths in Guaymas Basin, Gulf of California, J. Geophys. Res., 90 (4), 3075-3085, 1985.
Seitz, J.C., J.D. Pasteris, and I.-M. Chou, Raman spectroscopic characterization of gas mixtures. I. Quantitative composition and pressure determinations of CH_4, N_2, and their mixtures, Am. J. Sci., 293, 297-321, 1993.
Simoneit, B.R., P.F. Lonsdale, J.M. Edmond, and W.C. Shanks, Deep-water hydrocarbon seeps in Guaymas Basin, Gulf of California, Appl. Geochem., 5, 41-49, 1990.

Acknowledgements

We would like to acknowledge the work of the engineering team: George Malby, Mark Brown, and Danelle Cline; our collaborators at Washington University John Freeman, and Brigitte Wopenka; the captain and crew of the R/V Western Flyer; the pilots of the ROV Tiburon. Funding was provided by a grant to MBARI from the David and Lucile Packard Foundation; by the U.S. Dept. of Energy Ocean Carbon Sequestration Program (Grants No. DE-FC26-00NT40929 and DE-FC03-01ER6305); and by a grant from the Japan Society for the Promotion of Science.

Background Image: The 532 nm green laser of DORISS illuminates a cube filled with natural gas hydrate from a deep-sea gas vent at Guaymas Basin during the 2003 MBARI Gulf of California Expedition.