# Laser Raman Spectroscopic Instrumentation for *in situ* Geochemical Analyses in the Deep Ocean

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***Abstract*** **- Engineers and scientists at the Monterey Bay Aquarium Research Institute (MBARI) have successfully developed instrumentation for performing laser Raman spectroscopy in the deep ocean. Laser Raman spectroscopy is a form of vibrational spectroscopy that is capable of performing rapid, non-destructive, *in situ* geochemical analyses. The Deep Ocean Raman In Situ Spectrometer (DORISS) is based on a laboratory model laser Raman spectrometer from Kaiser Optical Systems, Inc. The sample is interrogated by a 532 nm laser and the Raman backscattered radiation passes through a holographic grating and is recorded on a CCD camera. Laser Raman spectroscopy is capable of analyzing a variety of solid, liquid and gaseous species. Due to the strict requirements for positioning the laser focal point when analyzing opaque samples, a Precision Underwater Positioning (PUP) system was built to position the DORISS probe head with respect to the sample. PUP is capable of translating the DORISS probe head in 0.1 mm increments with 1 mm repeatability.**

**DORISS and PUP are deployed by MBARI's remotely operated vehicles - ROVs *Tiburon* and *Ventana* - and are controlled by a scientist aboard the surface ship. DORISS and PUP have been deployed a number of times in Monterey Bay, the Gulf of California, and Hydrate Ridge, Oregon for testing and analyses of natural targets of interest. The development of smaller, second generation systems will allow DORISS and PUP to be carried on other deep submergence vehicles for use by the wider oceanographic community.**

## I. INTRODUCTION

Advancements in deep submergence technologies (e.g., remotely operated and autonomous underwater vehicles, and seafloor observatories) and new discoveries in the deep ocean have given rise to demands for new methods of *in situ* analyses. Acquiring data from deep sites without having to recover samples from every dive presents a new challenge to the technical oceanographic community. Many interesting science targets are not stable when removed from the pressure and temperature regime they are found in, such as high-temperature hydrothermal vent fluids and gas hydrates. In some cases, the goal is to observe a dynamic process and record the changes over time. Laser Raman spectroscopy is a technique capable of performing *in situ* geochemical analyses, which can analyze solid, liquid, and gaseous targets, as well as dynamic chemical processes in the deep ocean.

This paper will discuss the development, integration and successful deployments of a sea-going laser Raman spectrometer (DORISS – Deep Ocean Raman In Situ Spectrometer) and positioning system (PUP – Precision Underwater Positioner). DORISS/PUP have been deployed numerous times on MBARI's remotely operated vehicles (ROVs) *Tiburon* and *Ventana* (Fig. 1). Detailed specifications, design challenges, and science results are discussed along with future plans.

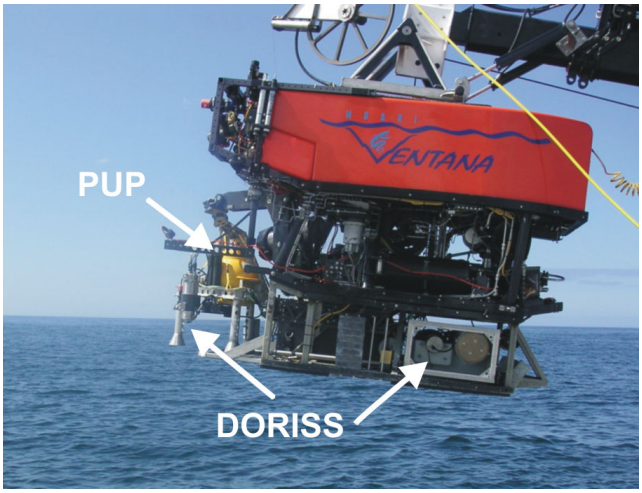


Fig. 1 – DORISS/PUP being deployed on the ROV *Ventana* in Monterey Bay

## II. RAMAN SPECTROSCOPY

Raman spectroscopy is a form of vibrational spectroscopy based on Raman scattering – the inelastic scattering of monochromatic light from a target molecule [1]. An incident photon exchanges energy with the molecule and is scattered with lower or higher energy than the incident energy (Fig. 2). The change in energy is equal to the change in vibrational energy of the molecule. The Raman spectrum therefore provides information about both the composition and the structure of the molecule.

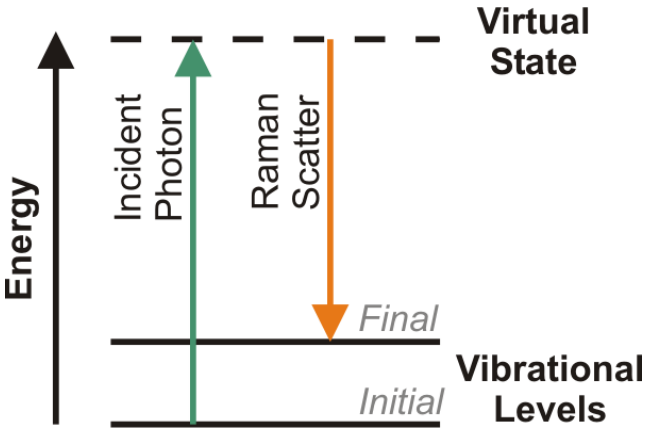


Fig. 2 – Energy level diagram of Raman scattering

Despite the fact that Raman scattering is a weak effect (only 1 in $10^8$ photons are Raman scattered), it is a potentially powerful analytical tool for deep ocean geochemistry. Raman spectroscopy is rapid, non-

destructive, and little to no sample preparation is required. Unlike IR spectroscopy, water does not cause major interference. The Raman spectrum of seawater consists of peaks from the bending and stretching of the water molecule, and a peak from the sulfate ion (Fig. 3). Most importantly, Raman spectroscopy is capable of analyzing solids, liquids, and gases.

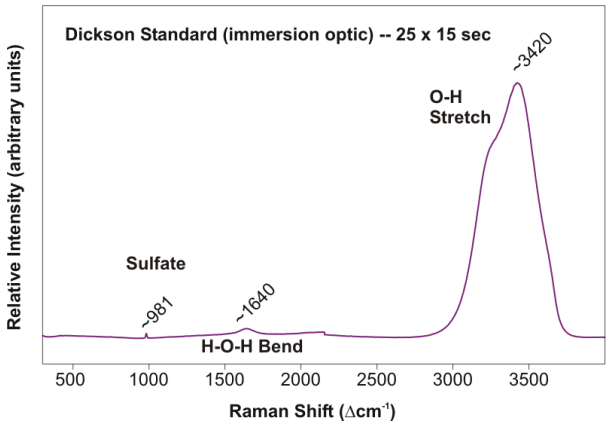


Fig. 3 – Raman spectrum of seawater [2]

A number of gases of interest to ocean scientists, such as carbon dioxide ($CO_2$), methane ($CH_4$), and higher hydrocarbons, are Raman active [3,4]. They can be analyzed as gases, in dissolved form or incorporated in clathrates. Raman spectroscopy is capable of distinguishing between structure I, structure II and structure H hydrate by observing the partitioning of gases into the different lattice cages (large and small) [5,6]. For targets such as gas hydrates, which have stability zones confined to the deep ocean, it is highly advantageous to be able to analyze them *in situ*.

Minerals and other solid targets can also be analyzed *in situ* using Raman techniques. Sulfides, anhydrite, calcium carbonates, silicates, feldspars, magnetite, and hematite are just some of the substances that are easily identified [7,8]. This alleviates the need for an excessive number of samples to be brought to the surface for shore-based analysis, and allows for *in situ* mapping of mineral distribution.

## III. DORISS DEVELOPMENT

Scientists and engineers at MBARI undertook the challenge of developing a laser Raman spectrometer (LRS) for use in the deep ocean [2,9]. Off-the-shelf technology was used to the fullest extent possible to prove the concept and manage risk. DORISS (Deep Ocean Raman In Situ Spectrometer) is based on a laboratory model LRS from Kaiser Optical Systems, Inc. (KOSI). The KOSI HoloProbe™ consists of a HoloSpec f/1.8i spectrometer with a duplex holographic grating, a 2048 x 512 charge coupled device (CCD) camera from Andor Technology, and a 532 nm Nd:YAG laser. The instrument was chosen for its resolution (~2-3 $cm^{-1}$) and spectral range (100-4400 $cm^{-1}$). The CCD camera selected has the option of being liquid cooled if the thermal conditions inside the pressure housing require additional cooling.

The instrument was divided into three pressure housings for use in the deep ocean to depths as great as 4000 m (Fig. 4). The electronics housing contains a single board computer, power components and the 100 mW 532 nm excitation laser (Fig. 5). Temperature and relative humidity sensors are present as well and are monitored continuously during a DORISS deployment. The housing is a glass filament reinforced epoxy construction that is slightly lighter and cheaper than a conventional aluminum or titanium design for the same 4000 meter depth rating. However, the reduced thermal dissipation capability limits the power-on time when the outside temperature is above 27° C.

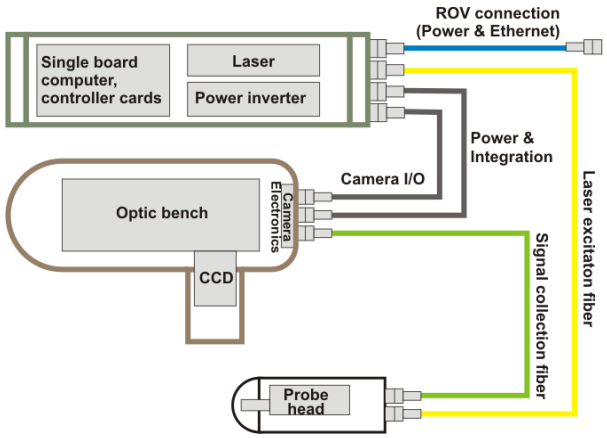


Fig. 4 - The conceptual configuration for the DORISS system

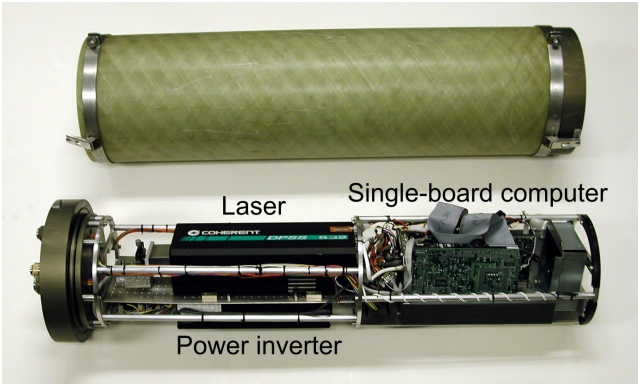


Fig. 5 – DORISS electrical housing and components [2]

The optical bench, CCD camera, and associated electronics are located in a separate housing (Fig. 6). The spectrometer housing was constructed of 7075 grade aluminum to minimize weight while taking advantage of the ocean's thermal capacity for cooling. To date, additional liquid cooling of the CCD camera has not been required.

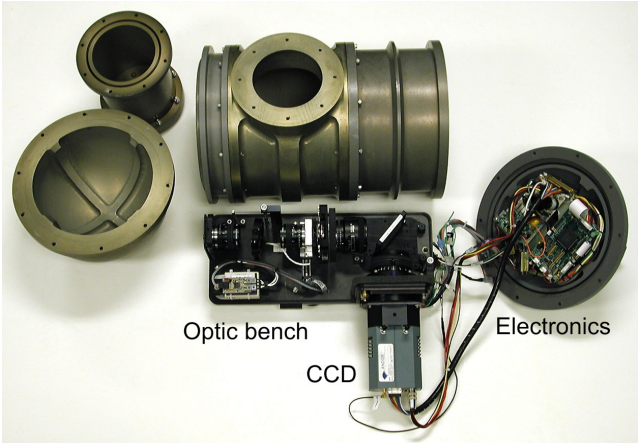


Fig. 6 - DORISS spectrometer housing and components [2]

The electronics housing (Fig. 5) and spectrometer housing (Fig. 6) are connected to each other with two cables providing power and communications between various components. These two housings are mounted in a drawer which is easily installed in the ROV toolsled (Fig. 1). A single connection to the ROV provides power and communications (Fig. 4).

The probe head housing contains the holographically filtered probe head which can accommodate a variety of sampling optics. The stand-off optic, as the name implies, allows the system to analyze a target without touching or entering the target material. The immersion optic is designed to be inserted into the target media. The stand-off optic is used behind a dome window, while the immersion optic protrudes from a flat endcap with a gland seal (Fig. 7). The off-the-shelf housing is constructed from 6AL-4V titanium and is small enough to be easily handled by the ROV manipulator. The probe head is connected to the laser and spectrometer via MBARI-built penetrating fiber optic cables.

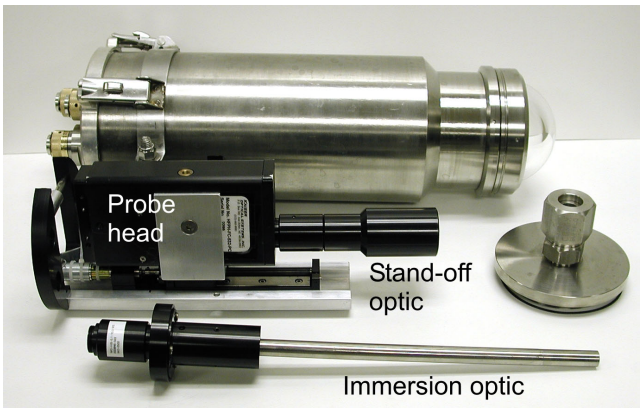


Fig. 7 – Probe head with sampling optics and pressure housing [2]

Beyond packaging, additional modifications were required for the system to be used in the deep-sea environment. Adjustments easily made in a laboratory had to be automated for remote operations. The thumb-screw optimization mechanism for the spectrometer slit was replaced with a remote motor stage (Fig. 8). Custom shielded cabling was incorporated to keep the low level CCD camera signals from being degraded. As noted above, custom fiber optic penetrators were also designed and manufactured at MBARI to reduce signal loss and stay within time and budget resources allocated for the project.

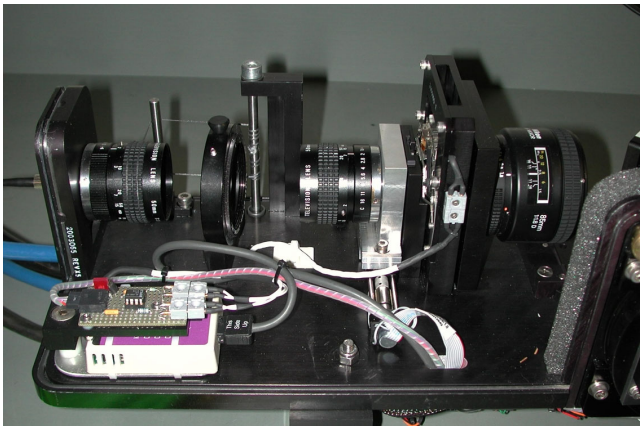

Fig. 8 – Optical bench with slit motor stage (center), water sensor, and temperature and humidity sensor (bottom left)

Power and communications for DORISS also required some customization. The ROV *Ventana* distributes 110 VAC for payloads while the deeper diving ROV *Tiburon* offers 240 VDC. The DORISS system was modified to be capable of operating from either power source. The instrument is controlled by a ship-board scientist via the Ethernet (10/100BaseT) protocol. MBARI engineering created an in-house connector standard for power and Ethernet that allows all payloads to safely connect to either ROV system.

## IV. PUP DEVELOPMENT

The Precision Underwater Positioner (PUP) was developed as a stand-alone system to meet the high precision positioning requirements of the DORISS instrument [10]. The focal depth of the DORISS probe head is very small. The laser spot size is on the order of tens of microns. Fig. 9 shows the focal depth of the two DORISS sampling optics determined using a polished silicon wafer as a target (the x-axis shows the distance from the focal point, and the y-axis shows relative intensity of the Raman signal). Intensity drops sharply at a focal distance beyond +/- 0.5 mm for the stand-off optic and +/- 0.1 mm for the immersion optic (Fig. 9). Therefore, the requirement was established for absolute positioning of 0.1 mm or better.

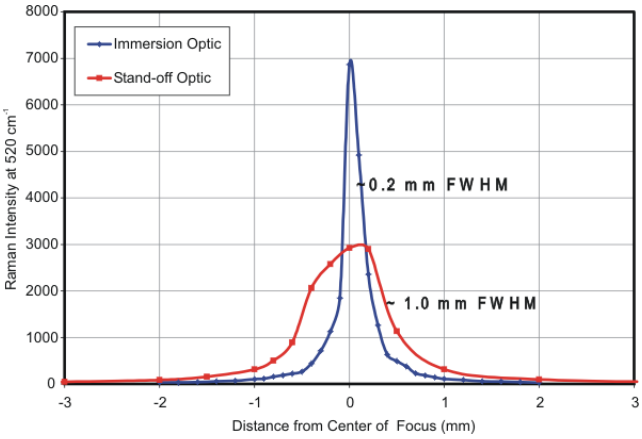


Fig. 9 – Focal depth of the DORISS optics [2]

Further requirements include the need to scan across or profile into samples. The system should be capable of tilting the probe head 45° in either direction to maximize the return from minerals in which sensitivity is dependent on incident angle. The useful working volume was specified to be at least 15 cm x 15 cm x 15 cm. The top level functional requirements are:

- Off-loadable from ROV
- Precision of 0.1 mm
- Stable throughout full range of motion and on varying seafloor surfaces
- Can pivot sensor head about a point
- Controllable by a shipboard scientist
- Stand-alone system capable of accommodating other instruments

The selected concept to meet these functional requirements consists of a tripod platform with 5 axes: a vertical axis, a horizontal axis, a rotational axis, and pan & tilt at the sensor head. Several aids were included to assist with positioning when PUP is placed a distance away from the ROV. These include a camera and light, and crossing

lasers mounted at the probe head. Due to time and resource constraints, a prototype with fewer degrees of freedom (DOF) and fixed legs was built for preliminary deployments (Fig. 10). Currently the PUP has 3 axes in place – vertical (Z), horizontal (R), and rotational (θ). These elements have been incorporated, fully tested, and deployed in science applications. The pan and tilt motion, and adjustable legs requirements have not been addressed at the time of this writing.

Following the same philosophical approach as the DORISS system, off-the-shelf components were used to the fullest extent possible. This approach resulted in savings on engineering time, ease of maintenance, and a more aggressive deployment schedule. The trade-off of this decision was increased weight, size, and power consumption.

The critical components for this system were the positioning devices, controller, and water-tight housings. The selected motors came from Exlar, a manufacturer of oil-cooled, high precision linear actuators. These oil-filled actuators were easily adaptable for high-pressure deep-sea applications. A custom manifold was designed and manufactured at MBARI that integrated the three standard connector openings from the manufacturer. The manifold allowed for a single connector thereby reducing the overall cost for underwater connectors, increasing the reliability by limiting the number of wet connections, and minimizing the number of cables between the various moving stages of PUP. The selected controller (Galil) matched the power rating for the Exlar motors and is capable of Ethernet communications. A Benthos glass sphere, commonly used for deep-sea applications, was selected for the pressure housing. The glass sphere was chosen primarily for cost and weight.

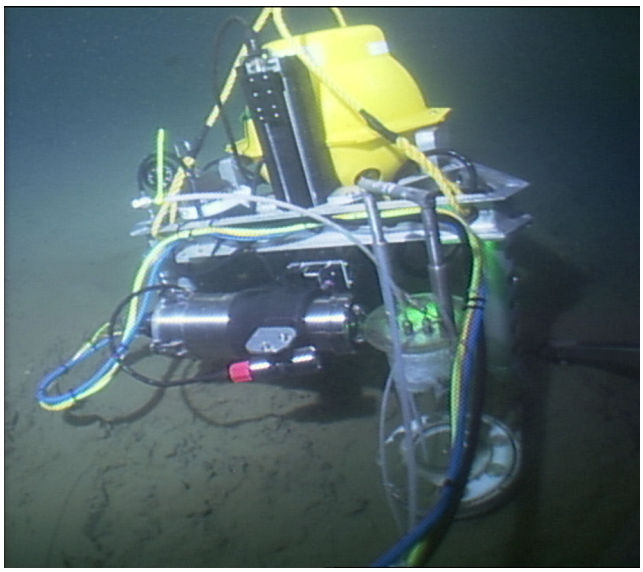

Fig. 10 – The PUP system with the DORISS probe head in a horizontal configuration looking at a sample cylinder with gas hydrate

## V. DORISS/PUP DEPLOYMENTS

Several engineering and scientific deployments have taken place over the past three years. These deployments have allowed us to gain experience and learn important lessons towards making the system robust. Additionally, a number of scientific successes have been achieved.

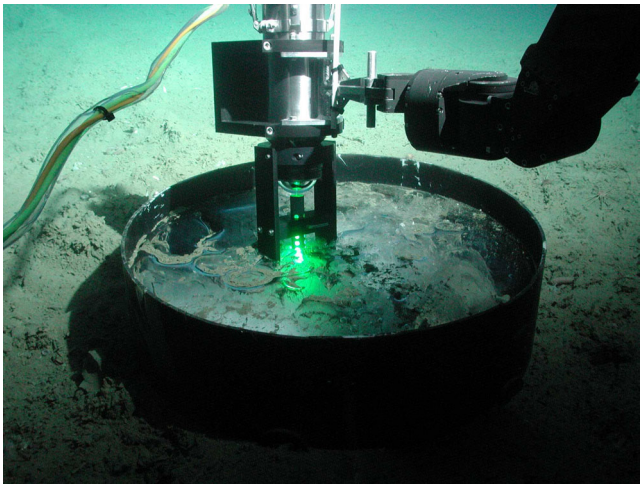

Fig. 11 – DORISS performing *in situ* $CO_2$ sequestration studies [10]

The first deployment of the DORISS system was in April of 2002 to a depth of 3607 meters in Monterey Bay (Fig. 11). Spectra of isopropanol, seawater, and calcite were taken to verify the performance of the system. Further experiments were performed in conjunction with $CO_2$ sequestration studies. Spectra of liquid $CO_2$ and dissolved $CO_2$ were obtained as part of the first *in situ* experiment performed by MBARI using laser Raman spectrographic techniques [11].

In the Fall of 2002, DORISS successfully performed an *in situ* gas dissolution experiment of a 50%-50% $CO_2$-$N_2$ gas mixture at 300 m depth. The DORISS system was used to observe the relative dissolution rates of $CO_2$ and $N_2$. The data showed the preferential dissolution of $CO_2$ into seawater [12].

DORISS was deployed as a part of a larger expedition of the R/V *Western Flyer* to the Gulf of California in May 2003. DORISS acquired the first *in situ* Raman spectra of natural targets in the deep sea. Gas was analyzed from a natural vent at 1582 m depth along a transform ridge north of Guaymas Basin (Fig. 12). Gas samples were also collected for lab analysis to verify the performance of the DORISS system. Raman spectra of the gas indicated that it was primarily methane. This result was supported by gas chromatography analysis in the lab which found the gas to be ~97% methane [13].

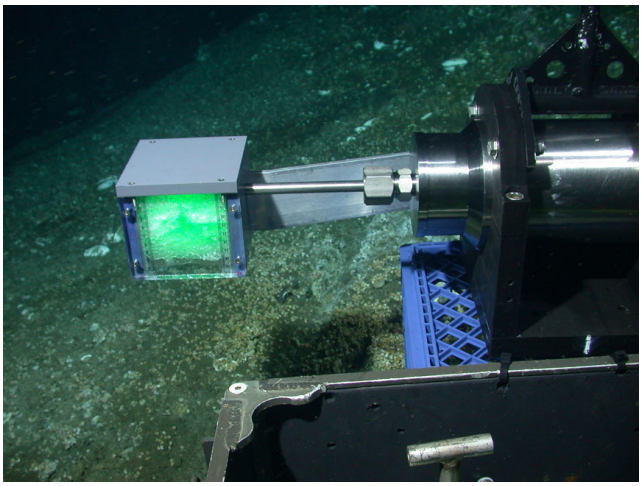

Fig. 12 – DORISS immersion optic penetrating the gas collection cube in the Gulf of California

Initial DORISS deployments focused on analyzing semi-transparent targets, which do not require precision positioning. The development of PUP provides the ability to analyze opaque targets. This greatly enhances the ability of DORISS to perform geochemical measurements in the deep ocean. As a demonstration of PUP's abilities, spectra have been collected from sub-millimeter scans across a granite sample deployed on the seafloor (Fig. 13). DORISS is able to analyze the individual mineral grains of the sample. By using PUP to move the DORISS probe head in a defined grid, and identifying the individual grains at each point, a point-counting technique [14] can be used to determine bulk rock composition.

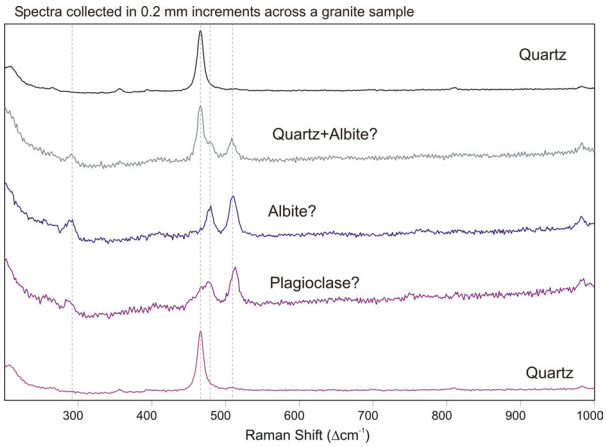


Fig. 13 – Raman spectra of a the mineral grains of a granite sample from sub-millimeter scans using DORISS/PUP

In December 2003 the DORISS/PUP system was used to collect *in situ* Raman spectra of gas hydrates in preparation for an expedition to Hydrate Ridge off the coast of Oregon. A sample of methane-ethane (80-20 mol%) hydrate was created *in situ* in a glass cylinder at 1022 m depth in Monterey Bay. With the DORISS probe head mounted horizontally on PUP (Fig. 10), quality *in situ* spectra were obtained of an opaque gas hydrate.

DORISS/PUP were recently deployed at Hydrate Ridge and Gorda Ridge off the coast of Oregon. At these sites, *in situ* Raman spectra were acquired of gas hydrates (Fig. 14), natural gas, hydrothermal vent fluids, hydrothermal minerals, and bacterial mats. Analysis of the data has just begun.

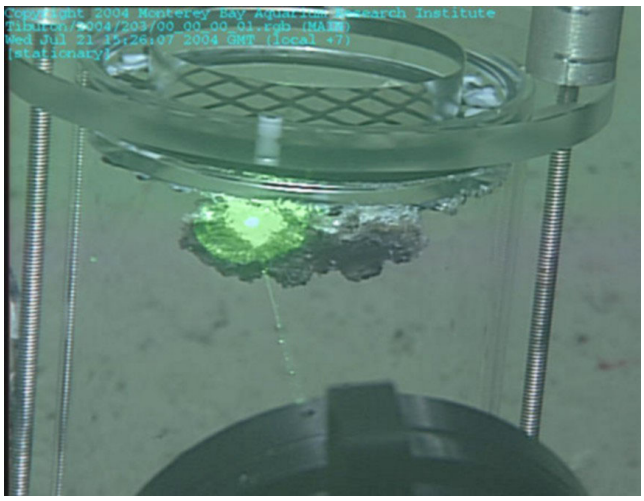

Fig. 14 – Natural hydrate sample illuminated by the DORISS excitation laser

## VI. CONCLUSIONS & FUTURE WORK

DORISS and PUP are prototypes developed to test concepts and to provide the preliminary deployments needed to understand how to build a more useful system. Both systems are very large and heavy and as such cannot be used on most deep submergence systems available to the oceanographic community.

Currently the DORISS/PUP design team is pursuing a decrease in overall system size and weight. The goal is to reduce the DORISS system to two housings by integrating new, smaller, off-the-shelf components from KOSI. It should be possible to develop a much smaller system with an estimated weight saving of at least 30%. Replacement of the single board computer with a PC-104 stack running Windows XP embedded™ is currently underway. The computer includes environmental monitoring, USB functionality, and more computational capability, all within a compact four card stack. Reducing the size of the optical head would also allow a corresponding size and weight reduction of the PUP system.

The DORISS/PUP system has the potential to be of great use to a wide variety of researchers. Our goal is to develop a compact and robust system capable of being deployed on a variety of deep submergence vehicles.

## ACKNOWLEDGEMENTS

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