Project Number: 600045

Project START: Jan 1, 2004 **Project Duration (in years): 2**

Project Manager: Bill Kirkwood
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Project Title:

Deep Ocean Raman In Situ Spectrometer (DORISS)

1) Abstract (new and continuing projects)

We propose first to complete and publish Raman work successfully initiated in the Gulf of California by comparing *in situ* and laboratory Raman spectra, and GC analyses of the same samples carried out within our Greenhouse Gases project. We propose to create and test new observing protocols for the analysis of geo-chemical solid phases through use of the PUP-DORISS combination with MBARI's ROVs. We plan to extend this important new capability to expeditionary work. We propose taking part in a Western Flyer cruise to northern sites in summer 2004. This will permit Raman studies at Hydrate Ridge, OR and at the Cleft segment. To date our work has primarily consisted of supporting the work of the Greenhouse Gases project. We are now ready to expand the usefulness of the DORISS by analyzing a variety of different targets in different deep-sea environments. We propose to use the PUP-DORISS system to carry out the first Raman measurements of a hydrothermal system (including vent minerals, hydrothermal fluids, and associated bacterial mats) in conjunction with the work of other MBARI researchers at the Cleft segment.

We propose to undertake several technical initiatives to accomplish science goals. First, we plan to complete the Precision Underwater Positioning (PUP) system. This is essential for the *in situ* Raman measurement of solids. We plan to enhance PUP with the other 3 axes (main stage rotation along with pan and tilt for the remote head) as identified in the Concept Design. We could not include this in 2003 due to resource limitations. Secondly, there are a series of upgrades required to correct limitations of the DORISS. These were discovered in field trials while performing engineering tests in the Gulf of California. The primary issue is sensitivity loss from attenuation in the external fiber optic cables. Testing verified that the current fiber optic cables are pressure sensitive and significantly diminish the optical signals. As a result the trace gas components from the major GoC gas vent were difficult to identify in the Raman spectrum, yet are known to be present at what should be detectable levels.

Other items include researching the possibility of changing to a much smaller probe head. This would make the DORISS-PUP combination much easier to handle and accommodate on other ROV systems. Through the lens (TTL) visualization was put on hold in 2003 for lack of resources. This will be carried forward but there are two possibilities: 1) replace the entire probe head and eliminate the need for TTL or 2) proceed with the delayed plans for TTL (should the smaller Raman prove invalid for our use). This would be accomplished as with the PUP design by appropriate trade studies and determining the best solution for MBARI. We are obtaining order of magnitude costs at this time, but it is difficult since our requirements are not for an "off the shelf" design.

The approach for the DORISS/PUP program in 2004 will be to outline the next multi-year elements for advancement. We will list our needs and prioritize them with the associated cost estimates and resource requirements. This plan will demonstrate the DORISS team understanding of what we are trying to accomplish, and the relationship of each technical element to the programs scientific goals. Using the previous programmatic success DORISS/PUP will propose the various elements in distinct groupings to optimize the management of resources.

2) Proposal

a) The problem addressed (for new projects only)

- Statement of the problem

While MBARI has already made important breakthroughs in carrying out the first deep-ocean Raman measurements, significant technical challenges still need to be addressed to fully implement the DORISS instrument. We still have difficulty obtaining Raman spectra from opaque targets. In early experiments on large transparent targets we have positioned the laser with an ROV robotic arm. Arm vibrations and drift have not been important in those cases, but this technique cannot be used for opaque materials which have stricter positioning requirements. Precise focusing of the laser spot on the target surface is required when analyzing opaque targets. This is beginning to be addressed by the partially completed precision underwater positioning system (PUP). We currently have designed, built, and tank tested a 2 DOF prototype of the PUP to solve this problem. PUP still needs the additional three axes that we could not afford in 2003. By mounting the Raman probe head onto the PUP, which is off-loaded from the ROV, the required precision and stability is achievable, as we will be proving during test dives in late August of 2003. Another challenge to overcome is the size of our Raman system. The size must be reduced and the system must be lighter and easier to integrate with other deep submergence assets (e.g., the ROV Jason II, and possibly the submersible Alvin) to be of use to the broader oceanographic community.

We propose to advance the DORISS program by making the first *in situ* field measurements of sulfide minerals, carbonates, and bacterial mats. We also propose to further develop, improve and make known the capabilities of Raman spectroscopy to the ocean science community. We plan to modify the DORISS system so that it is more easily used by our own ROVs as well as other support vehicles by constructing a properly configured deep sea instrument concerned with weight and size issues. We also propose to enhance our laboratory capabilities such that calibration and operational protocols can be refined, and analyses of standards can be performed for proper correlation with seafloor data. This will prove the validity of the DORISS system as a significant sensor for the greater ocean science community.

- Why it is important

Raman spectroscopy is a useful technique for ocean science for a variety of reasons. Advantages include little or no sample preparation; it is rapid, and non-destructive; and it is applicable to solids, liquids, and gases. Water, through which most ocean measurements must be made, is Raman active but does not cause major interference. There are a number of critical issues in ocean science that can be addressed by the use of Raman spectroscopy. Raman studies have been made of the aqueous CO_2 system in the laboratory [*Abbott et al.*, 1982] that are of particular interest to the health of the World's oceans and to society in general. Seafloor gas hydrates are of great interest for their potential as an energy source, their potential to destabilize the seafloor, and their possible contribution to climate change. A number of laboratory studies using Raman spectroscopy have been performed on both CO_2 and CH_4 hydrates revealing structural information, and details of cage occupancy [*Subramanian and Sloan*, 1999; *Sum et al.*, 1997]. Recent work indicates that hydrates formed in seafloor sediments may differ significantly from those created in the laboratory [*Huo et al.*, 2003]. The ability to analyze gas hydrates *in* *situ* via Raman spectroscopy will greatly increase our understanding of these important constituents of the marine geosphere.

- How it relates/contributes to MBARI's mission and strategic plan

The significance of the DORISS work is to provide the currently unavailable ability to perform *in situ* analyses of unaltered deep sea targets. This effort is part of the MBARI goal to development instruments for the advancement of ocean science. The DORISS system will help to increase the effectiveness of remotely operated vehicles by allowing them to perform detailed *in situ* analyses, rather that serve as mere collection devices.

Additionally there is active interest by the Southampton Oceanographic Center (SOC) to have collaborative efforts with MBARI regarding DORISS and in situ Raman spectroscopy. Researchers at SOC have inquired with Kaiser (the vendor supporting MBARI) about purchasing the components to build a similar system to ours. SOC has also taken delivery of a Jason II vehicle platform. We believe that assisting to the extent possible with the transfer of DORISS technology to another oceanographic institution (based on future discussions with outcomes as yet undetermined) is ultimately contributing to MBARI's overall stated mission "... MBARI is to achieve and maintain a position as a world center for advanced research and education in ocean science and technology, and to do so through the development of better instruments, systems, and methods for scientific research in the deep waters of the ocean."

b) Approach to the problem (new and continuing projects)

- Engineering/technology development

<u>DORISS</u>

DORISS (Deep Ocean Raman In Situ Spectrometer) is based on a laboratory model laser Raman spectrometer from Kaiser Optical Systems, Inc. The Kaiser instrument was chosen for its resolution, wide spectral coverage, and few moving parts. However, some components proved to be less than robust when deployed in the ocean (being subjected to mechanical vibrations and rapid changes in temperature). Two critical alignment mechanisms — the laser-fiber alignment mechanism, and the spectrometer slit alignment mechanism — were therefore modified at MBARI.

The Kaiser instrument was divided into three pressure housings for deep-sea deployment. The spectrometer and camera electronics are in an aluminum housing, custom designed to accommodate the factory L configuration with the camera at a 90-degree angle to the optical bench. The electronics housing contains the laser, power inverter, and a single-board computer with PCI controller cards. The laser and spectrometer are connected via 7 m long, pressure-tolerant fiber optic cables to a remote probe head housed in a titanium pressure case. The custom-built, penetrating fiber optic cables experience pressure-induced attenuation and need further development. The probe head is positioned at the target of interest by the ROV manipulator while the spectrometer and electronics housings remain fixed in the toolsled.

Although DORISS has proved successful to date, a number of important improvements are required to expand its usefulness. Primarily it must be reduced in size and weight to increase it's overall functionality and be accommodated on other platforms which will lead to being accepted by the larger oceanographic community that is expressing interest at the moment. Additionally, experience has shown that the system is difficult to configure and maintain at sea. We will research options (both off-the-shelf, and custom-designed) for decreasing the size and weight of the present system. For example vendors are currently developing new, smaller and more robust components that we can use in our system. Custom modifications can also be done to reduce the overall size of the present instrument.

PUP

A key advantage of DORISS over other analysis techniques is the ability to non-destructively analyze a specimen *in situ* without sample preparation or alteration. In order to maintain the experimental flexibility that DORISS provides, we have devised a means of accurately placing the laser spot on an undisturbed oceanic sample. We have made advances in obtaining spectra from opaque targets by developing a precision underwater positioner (PUP).

PUP will be a 5-degree of freedom (DOF) positioner consisting of Z, R, and θ axes and a pan & tilt device at the sensor head, of which the 2 primary axes are already built. It includes a video camera and crossing lasers that provide the user assistance in positioning the system. The DORISS probe head is mounted to the PUP, which is off-loaded from the ROV to decouple it from ROV induced motion/vibration. The current electro-mechanical actuators move the probe head with a precision of 0.1 mm and a repeatability of 1 mm. The addition of the pan and tilt device will allow the laser beam to be pivoted about a point to find the optimum angle for maximum signal return [*Kirkwood et al.*, 2003 (in pres)]. We are using a conservative, incremental approach to provide the minimum necessary axes for obtaining preliminary DORISS data on the seafloor while verifying the remaining functions of the PUP. The 2 DOF PUP will be used at sea during the second half of 2003, and the full 5 DOF PUP should be completed for cruises in 2004. With the improvement in DORISS size and weight the PUP can also be made smaller and lighter since it is sized to fit the DORISS remote head. This has the advantage of minimizing ROV payload for at sea operations, making operations easier and allowing for other science activities to take place on the same dive – something the current DORISS and PUP combination cannot accommodate.

- Field programs

Previously, the DORISS project used a limited number of engineering dives in 2002 to test the DORISS system and determine necessary modifications. These dives proved that accurate Raman measurements can be made in the deep ocean [*Brewer et al.*, 2002a]. Measurements were made of known samples and standards to characterize the behavior of the instrument under deep-sea conditions and to verify the ability to analyze a range of targets (solids, liquids, and gases). Fluorescence was thought to be a major impediment to *in situ* Raman analyses in the ocean. While significant fluorescence was observed in the Raman spectra obtained shallower than 200 m depth, spectra from the deep ocean were free of fluorescence despite the presence of marine snow.

DORISS was also deployed as auxiliary equipment in conjunction with science experiments related to CO_2 sequestration studies. These dives provided us with the opportunity to collect spectra from liquid CO_2, gaseous CO_2, and dissolved-CO_2 enriched seawater. Measurements were also made *in situ* of the relative dissolution rate of CO_2-N_2 gas mixtures, thus illustrating the preferential dissolution of CO_2 into seawater. The expedition to the Gulf of California in 2003 afforded us the first opportunity to collect *in situ* Raman spectra of natural targets —

natural gas (primarily methane) exiting the seafloor and natural gas hydrates. Collecting a gas sample suitable for Raman analysis proved difficult because the gas formed hydrate on contact with the Raman probe tip. Despite the difficulty, we were able to obtain spectra of the gas showing methane peaks and additional constituents. We were unable to obtain spectra from gas hydrates *in situ*; the key problem encountered was that of positioning the probe head. It was this acknowledged technical difficulty that led us to develop the PUP system.

For 2004, we propose to continue a program of coordinated laboratory and field measurements that will expand and demonstrate DORISS's usefulness as an *in situ* instrument for the deep ocean.

<u>Laboratory Program</u>

Detailed laboratory work is needed to better understand the Raman signatures of ocean targets (e.g., seawater, natural gases, hydrothermally altered fluids, and seafloor and hydrothermal minerals). Raman spectra can be difficult to decipher in the field, and when signals from a variety of molecules are superimposed it can be difficult to interpret the combined signal. Raman scattering efficiencies also vary from substance to substance, so one cannot easily infer relative concentrations of constituents by their relative peak heights in raw spectra. Nonetheless the power of this technique lies in its unique ability to differentiate mineral isomorphs (e.g. calcite versus aragonite, oxidation states etc.). For this reason it is important to analyze specimens in the lab that one expects to encounter in targeted natural environments. Developing a database of oceanic relevant spectra is an important first step to a successful field program.

Temperatures and pressures of the deep ocean accessible to MBARI's ROVs can reach as low as ~1.5°C and ~40 MPa. Both temperature and pressure can have a significant effect on Raman signal — altering peak shapes and shifting peak positions. We will use a pressure cell with an optical window to obtain Raman spectra of gases at high pressures in the lab. Some Raman-active gaseous species that we expect to encounter in hydrates and hydrothermal environments include CO_2, CH_4, and H_2S. It will be necessary to analyze these species both as gases and in dissolved form to understand how their spectra vary in different phases, as gaseous vs. dissolved, at different pressures, and what concentrations our system can detect.

A number of minerals that are Raman active are present in hydrothermal systems. These include pyrite, sphalerite, anhydrite, etc [*Pasteris*, 1998]. Minerals that make up basaltic rocks are also Raman active (e.g., pyroxene, plagioclase, feldspar, etc.). Researchers at Washington University have performed Raman analyses of weathered basaltic rocks [*Wang et al.*, 1999] and lunar samples [*Haskins et al.*, 1997] to demonstrate the usefulness of Raman spectroscopy on future Mars missions . We will similarly analyze a number of seafloor rock samples in the lab in preparation for field deployments.

<u>Ocean-going Program</u>

During the summer of 2004 we propose to participate in an MBARI expedition to the Juan de Fuca Ridge, and to Hydrate Ridge, on the R/V *Western Flyer*. It is our goal to make fundamental measurements of selected targets at each site. Previous visits to Hydrate Ridge have revealed the presence of free gas, and of large crystalline chunks of solid hydrate [*Brewer et al.*, 2002c]. With the use of the Precision Underwater Positioner (PUP), we plan to obtain the first *in situ* spectra of gas hydrates. Hydrothermal environments consist of a variety of targets that are capable of being analyzed by Raman spectroscopy – hydrothermal fluids, chimney minerals, and bacterial mats. Due to the high temperatures of the exiting hydrothermal fluids (up to ~400°C) a new titanium immersion optic will be obtained for working in vent fields.

A number of cold seeps and bacterial mats are present in Monterey Bay. These sites are accessible via the R/V *Point Lobos*, and we will make exploratory Raman measurements at these sites in conjunction with other MBARI scientists (e.g., Jim Barry).

- Data reduction and analysis

Data analysis and reduction will be achieved by comparing the *in situ* spectra with laboratory results on recovered samples where possible. This will permit examination of any instrument artifacts at depth. Standard software packages such as GRAMS allow us to easily share spectroscopic data. We intend to publish the results of the work in academic journals and to present our findings a national meetings.

- Proposed duration of project and approximate plan of action

The DORISS system has the potential to be of great use to a wide variety of researchers. It is capable of analyzing solids, liquids, and gases in a point-and-shoot manner. Its broad spectral range makes it appropriate for low-wavenumber Raman scatterers such as sulfur and sulfur containing minerals, mid-range scatterers such as CO_2, O_2, and N_2, and high-range scatterers such as clathrate hydrates, and hydrous minerals. All of the aforementioned targets were identified as important and in need of further instrument development at the NSF sponsored "Next Generation Biological and Chemical Sensors Workshop" held at WHOI in mid-June of 2003. Thus DORISS is recognized as a useful cutting edge analytical tool and survey instrument. DORISS can also be adapted to study a particular target or process in greater detail by changing the grating to cover a smaller spectral region with higher spectral resolution, making it an even more versatile tool.

We propose to further develop DORISS into a more useful geochemical tool for the broader oceanographic community through a program of coordinated laboratory and field measurements. Previous work has shown that laser Raman spectroscopy has important potential for deep-sea studies. To date DORISS has been primarily an engineering effort and we propose to expand the science role in the coming year. The next step is to move beyond the development phase into a scientific operational phase while making significant improvements to the at sea DORISS components.

c) Specific deliverables (new and continuing projects)

- Products from research and development (instruments, tools, documentation, publications, presentations, etc.)

This proposal calls for a cruise to Hydrate Ridge and the high-temperature hydrothermal vents on the Cleft Segment of the Juan de Fuca Ridge for DORISS field work in August/September 2004. Deliverables will include the executed field measurements at these sites, and presentations on the data at national meetings and journal publications in 2005. In addition there will be the appropriate technical papers based on the performance upgrades to DORISS and the PUP system.

Technical products and accomplishments will include an upgraded and improved DORISS system that corrects the optical fiber attenuation flaws found in pressure testing and field experiments. The new components and design work will make the at sea version easier to use and allow the older components to be used for laboratory work, fulfilling the need for a laboratory system with minimal cost. Based on resources available, the PUP system will be completed in 2004 and modified slightly to take advantage of the reduced weight and size of the improved DORISS system. In addition a technical paper is expected to be published in time for Oceans 2004 detailing the advancements made.

- How success will be measured

The project schedule and work breakdown structure clearly outlines milestones for the listed items. The project will measure success by publication of the data collected form field programs and compared to lab experiments. Success will also be measured through the proper management and prioritization of stated goals contrasted against awarded resources. The goal being to maximize the scientific returns from the overall milestones as stated (or revised upon approval or resources). Please see outlined milestones at the end of this proposal.

d) Project team (new and continuing projects)

The expectation is to keep the current DORISS/PUP team intact to the extent possible. This would include Ed Peltzer, Sheri White, Mark Brown, Richard Henthorn, and Scott Jensen. The exact amount of time for each member will vary from last years requirements (as outlined in the resource section). New post-doc Rachel Dunk will also be added to the team. We plan to continue with the outside collaborators from U of Washington (Jill Pasteris) and to make use of the technicians as much as possible (John Ferreira for example).

e) Project Lab Space (new and continuing projects)

The team is currently able to function in the lab space provided however two problems exist. Solving these problems would be beneficial for the DORISS program and potentially other science lab users. The first concern is the use of medium power lasers in close proximity to three other operating lab groups. Although the DORISS team is cautious and warns other lab users of the dangers, the potential exists for an accident involving unintentional laser contact with eyes. This could be minimized by any number of options, including some screening of lab space, interlocks, or moving to another location. The second concern is the need for a lab unit for laboratory experiments and verification of the sea-going DORISS results. This requires more bench top space. The current lab is an ideal for location with power and network connections that work well for us. The current proximity to Dr. Kolber's lab is also expected to help foster collaborations as time progresses. The preferable (and proposed by the DORISS team) solution is to rearrange the current lab space to be more functional and put up barriers to protect the innocent passerby. It would be nice to expand into the current SideARM working area since that program is expected to slowdown hardware development and space needs will be reduced.

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3) Budget Justification (new and continuing projects)

DORISS Upgrades

1) Optic bench (spectrometer housing)
   – replace w/ new linearized bench with lighter base plate
      RATIONALE: smaller, lighter, easier to package
      TIMING: as soon as possible
      COST: ~$20,000 (based on cost of current optic bench)

2) Laser (electronics housing)
   – replace w/ new Invictus or a smaller option after a market search
      RATIONALE: built-in diagnostics, electronic "shutter",
         Coherent is no longer supporting our laser
      TIMING: as soon as available (~6 mo to 1 yr)
      COST: $24,000 (Kaiser quote)

3a) CCD camera (spectrometer housing)
   – replace w/ new Andor camera
      RATIONALE: A/D converter incorporated into camera (no PCI card),
         USB capability, smaller over all package
      TIMING: as soon as available (~1 yr)
      COST: ~$24,000 (based on cost of current camera)

3b) Onboard computer (electronics housing)
   – replace single-board computer with PC-104 stack
      RATIONALE: smaller, USB capability to support new Andor camera
      TIMING: needs to be done after obtaining USB-compatible camera (~1 yr)
      COST: ~$3000 (estimate from Rich Henthorn)

4) Probe head (probe head housing)
- replace w/ new MR probe
  - RATIONALE: smaller, lighter
  - TIMING:as soon as possible
  - COST: $9,950 (Kaiser quote) [funding requested through NSF proposal]
- add neon bulb in housing
  - RATIONALE: provides calibration capability during deployment
  - TIMING: as soon as possible
  - COST: $395 for calibration-quality neon bulb (Kaiser quote)
- new titanium immersion optic
  - RATIONALE: shorter is easier to handle,
    fixed focal distance less likely to become misaligned,
    allows working in high-temperature hydrothermal vent environments
  - TIMING: as soon as possible
  - COST: $6,000 (Kaiser quote) [funding requrested through NSF proposal]

4) Milestones (new and continuing projects)

	Milestone 1	Milestone 2	Milestone 3	Milestone 4	Milestone 5	**Total Resources** [1] for each resource category for all milestones listed here
Milestone date	1st qtr 2004	1st qtr 2004	2nd qtr 2004	3rd qtr 2004	4th qtr 2004	
Milestone description	Research and Review PUP and DORISS, add GUI features	Order smaller components and PDR for DORISS Upgrades	PUP PDR and modifications base don the DORISS selected upgrades	Hydrate Ridge cruise preparations, testing, cruise, and logisitcs	Data reduction and technical publication / presentation (IEEE/Oceans)	
EE	10	10	10	15	5	50
SE	30	30	20	20	10	110
ME	20	40	50	30	10	150
IAG						
Machine Shop			50			50

[1] This number should be same as the number you entered on the resource requests for this particular resource