Project Number: 600045

Project START: Jan 1, 2003 **Project Duration (in years): 2 years**

Project Manager/PI: TBD/Peter Brewer

Project Title: Laser Raman Spectrometer

2003 Proposal Form – Internal-only Projects

1) Abstract (new and continuing projects)

The LRS project has successfully completed the first 3-year phase, and a second 2-year project is proposed here. In Phase 1 (Yr. 1) we accomplished specification, vendor search/testing, and acquisition. Yr. 2 saw design, fabrication and MBARI testing, and by mid-year of Yr. 3 we have carried out 5 successful ROV deployments (using both Tiburon and Ventana) to a maximum depth of 3600 m. A first paper has been submitted, and two more are underway. We have successfully initiated *in situ* calibration protocols, and can now return spectra of exceptional quality from the deep ocean.

Our overarching goals for Phase II are first to make innovative scientific use of the system we have created, second to enhance the system to achieve its full potential, and third to explore future development of lighter, smaller, robust systems for use on other platforms in the community. The development of a critical positioning system is already planned for the second half of 2002. Three more Ventana dives and one Tiburon dive are scheduled for LRS science/technology in late 2002, including deployment of a new optical lens for the probe head.

In 2003 we plan on using the LRS in the Gulf of California for gas vent/hydrate science, and if possible at a hot vent site. In local waters we plan on using the instrument in an international CO_2 sequestration experiment with Japanese and Norwegian colleagues, and to initiate measurements on novel targets such as bacterial mats and in pore waters. These will be challenging. We also plan on a series of laboratory measurements with a small sample pressure vessel to ensure adequate knowledge of spectra obtained *in situ*: the Raman signal detects solution speciation, and chemically sophisticated approaches are required.

A number of engineering enhancements must be made to the LRS. Through-the-lens (TTL) visualization is required so that the target being measured can be clearly identified. This is standard in laboratory instruments. It requires a movable beamsplitter in the optical path. We expect that the camera system available from Kaiser can be adapted for our system. A new and larger probe head pressure case will be required to accommodate this unit. The sample must be illuminated by white light, either with an external LED ring, or by using a beam splitter in the optical path, as is standard with reflected light microscopes. The laser beam has sufficient power to dissociate hydrates, or to photo-bleach targets, and thus a controllable light shutter will be added to the optical path. For signal enhancement in sea water we will explore both a Teflon capillary waveguide (liquid core optical fiber – LCOF), and silver surface enhanced Raman scattering (SERS) techniques, for 2004 implementation.

We will need two trips each consisting of two dive days to accomplish all of the science and engineering goals that we have planned for 2003. Engineering validation and verification of the XYZ positioner and the TTL visualization system will each require two dive days on separate trips. Science experiments will also be conducted throughout the year.

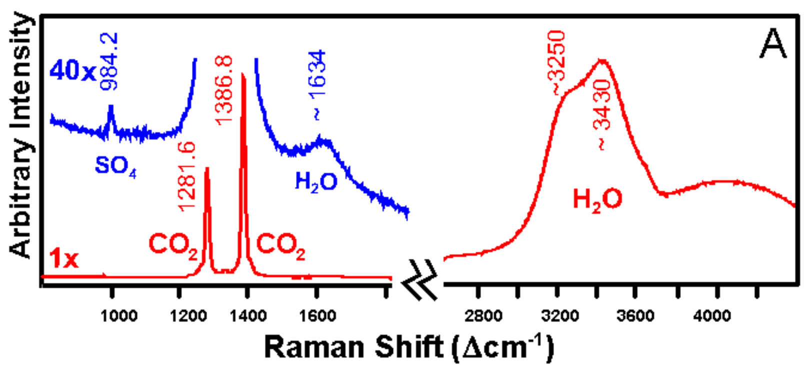
In 2004 we will propose to use the instrument at northern hot vent sites for *in situ* measurements of vent plume and mineral geochemistry. Possibilities for future lighter, smaller instruments include the Wang/Haskins Mars Explorer design at Washington University, and the NATO sponsored IFREMER unit, scheduled for evaluation in 2004.

2) Proposal

a) The problem addressed (for new projects only)

MBARI's mission includes "development of better instruments, systems, and methods for scientific research in the deep waters of the ocean." The Laser Raman Spectrometer (LRS) is a prime example of a cutting-edge instrument adapted for use in the ocean which allows new measurements to made in a number of different fields (e.g., chemistry, mineralogy, and biology). While Raman spectroscopy is not a new field, technological advances such as solid-state lasers and charge-coupled device (CCD) cameras have improved the sensitivity and robustness of the technique. It is particularly useful with remotely operated vehicles (ROVs) because it is small enough to be carried to the seafloor, powerful enough to interrogate most targets of interest, and no sample preparation is necessary – allowing *in situ* chemical characterization of objects on the seafloor.

The LRS uses a 532 nm laser to excite a sample of interest and then records the Raman (inelastically) scattered light. When monochromatic light is incident on a sample, most of the energy is scattered elastically – at the same frequency as the incident light. However, some of the energy (1 in 10^8 photons) interacts with the molecules of the sample and is scattered at a shifted frequency (inelastically scattered). The frequency shift from the exciting wavelength is due to the characteristic molecular vibrations of the molecule. So the Raman spectrum serves as a kind of "fingerprint" of a substance based on both composition and molecular structure. Raman spectroscopy can be used to study gases (e.g., CO_2, CH_4), liquids and dissolved species (e.g., isopropanol, and CO_2 or SO_4 in seawater), solids (e.g., precipitates, particles, minerals), and phase transitions (gas/liquid, and gas/solid are spectrally distinct).



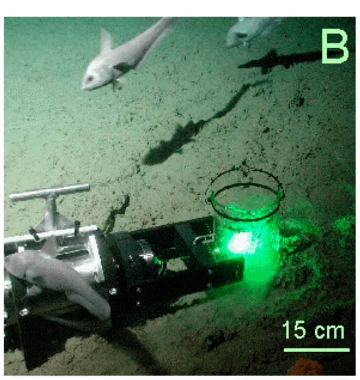


Figure 1. A) Raman spectrum of liquid CO_2 placed directly on the seafloor (image not shown). The two strong bands of the Fermi diad of CO_2 can be seen above the background spectrum of seawater —the H_2O bend (~1630 Δcm^{-1}), O-H stretch (~3400 Δcm^{-1}), and S-O stretch (~984 Δcm^{-1}; bulk sea water SO_4^{2-} concentration is about 28 mM). **B)** The LRS probe head positioned at a 4 liter beaker of liquid CO_2 on the seafloor at 3607 m depth, 1.5°C.

During the initial three-year project, the LRS has successfully been deployed on both Tiburon and Ventana to make measurements of CO_2 as a gas, in liquid form (Figure 1), and incorporated in hydrates. Initial measurements of minerals (calcite, dolomite, limestone, and serpentinite) have been made, as well as profiles of the water column. These measurements of pure samples taken to the seafloor simply serve as a test of the sensitivity and versatility of the instrument. The next step is to take the LRS to unique environments to make measurements of naturally-occurring targets on the seafloor – CO_2 and CH_4 hydrates, gas vents, and hydrothermal fluids and minerals.

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

While we initially planned for a three-year project to continue LRS work, the Management Team has recommended this proposal be limited to one year. We recognize that engineering resources are limited and that there is a push to complete the development phase of projects such that they can be transitioned into operations. However, adapting an instrument for use in the ocean is often an iterative process. Cruises throughout the year are necessary to test enhancements made to the instrument. Also, by deploying the instrument to make a variety of scientific measurements during the development process, we learn what additional enhancements are needed to make the LRS a highly functional scientific instrument. Therefore, we request that consideration be given to supporting the LRS for two years. While one year would allow us to add TTL visualization, adapting additional techniques such as SERS and capillary waveguides (which will increase the sensitivity and flexibility of the system) will require a second year. Additionally, the second year would give us the opportunity to use the LRS to make measurements of high-temperature vents on the Juan de Fuca Ridge, which is of interest to other scientists (such as D. Stakes) and will show the usefulness of laser Raman spectroscopy in other disciplines and environments.

In Phase I, a laser Raman spectrometer was acquired from Kaiser Optical Systems, Inc (KOSI). and adapted for used in the deep-ocean. Adaptations included dividing the components up into three pressure cases, building penetrating fiber optic cables, and developing an Ethernet interface to control the system from the shipboard control room. During testing of the instrument, it became apparent that certain components were not robust enough for ocean deployment and were redesigned and rebuilt. The slit optimization mechanism is being replaced with a motorized stage that can be controlled remotely. The laser injector is being rebuilt to use uncoupled XYZ movement for focussing the laser into the fiber optic cable. Additional features were also deemed necessary and are being added to the system: a diamond standard inside the probe head as an internal calibration reference; and a one-dimensional linear translational stage inside the probe head pressure case for fine focussing of the 2.5” stand-off optic. Design and construction of an external XYZ precision positioner has also begun. Integration and testing of the XYZ positioner will occur in early 2003.

Engineering improvements to be made in Phase II are primarily to improve operations of the system:

- Through-the-lens (TTL) visualization is the top priority for 2003. Because of the small focal volume of the laser, positioning is very important for making detailed measurements. In order to fully use the precision provided by the XYZ positioner, through-the-lens visualization capability is needed. This will consist of adding optical components to the probe head which will require a larger pressure case. KOSI has such a system for the laser Raman microprobe (the standard probe head is integrated with a microscope unit). It is believed that this system can be adapted for our instrument in 2003. Essentially a moveable beamsplitter is inserted into the optical path between the probe head and the optical lens. This allows the scene (with the laser spot) to be imaged by an additional camera. The LRS control software (HoloGRAMS) provided by KOSI is designed to handle this added functionality.

- Currently, the only species dissolved in seawater that the LRS is capable of detecting is SO_4 (28 mM). The sensitivity of the instrument to species dissolved in a fluid can be increased with the use of liquid core optical fibers (LCOF) — Teflon capillary waveguides. LCOFs can lead to an increase in sensitivity by a factor of 10^3 (Altkorn, 2001). This would allow measurements to be made of the CO_2 system in seawater (with direct sensing of the HCO_3^-, CO_3, and CO_2 peaks) and of dissolved species in hydrothermal vent fluids. Sensitivity increases may also be obtained by surface-enhanced Raman scattering (SERS). The development of the hardware and methods necessary to use LCOF and SERS will be completed in 2004.

- Some of the targets to be analyzed with laser Raman spectroscopy can be damaged (photobleached) or altered (CO_2 hydrates melted to liquid CO_2) by long exposure to the 30-40 mW laser used by the LRS. Therefore, a laser shutter must be added to the new laser injector. The new injector design accommodates this addition and the LRS control software (HoloGRAMS) is capable of laser shutter control. This will also increase the safety of the instrument by allowing the laser beam to be blocked while the instrument is powered on for communications testing and calibration on deck. This is an important addition we hope to have in place by early 2003.

- The throughput of the current fiber optic cables running to and from the probe head appears to be slightly sensitive to changes in pressure. Because of this effect and the fragility of the cables, new armored cables should be obtained. As the current cables are functional, this is not a top priority, and will be addressed in 2004.

- In order to make the LRS more useful to a variety of researchers, we will look into the development of a smaller, more robust system. A significant decrease in size of a laser Raman spectrometer has been accomplished by Wang and Haskins at Washington University in St. Louis for use on a Martian surface explorer (Wang, et al., 1998). In 2004 we will evaluate ways to reduce the size of the system, both by repackaging current components and by obtaining or designing smaller components. This will allow the LRS to be used on other platforms in the oceanographic community (e.g., Alvin) that have smaller payload capacities. Also, the ability to take down an smaller LRS that can be used in addition to other instruments and sampling will make the LRS more appealing to researchers (e.g., biologists and geologists) who may benefit from its capabilities. Scientists such as D. Stakes (MBARI), D. Kelley (Univ. of Washington), and P. Girguis (MBARI) have all expressed interest in the LRS and using it to characterize the environments they study – hydrothermal vent environments and pore waters.

Scientifically, Phase I primarily consisted of making measurements of pure substances taken to the seafloor (liquid CO_2, CO_2 hydrate, various minerals, etc.). This allowed us to refine the techniques necessary to collect good quality spectra in the ocean. In Phase II we propose to use the LRS to look at new ocean systems and make innovate use of the instrument. The capabilities of the LRS will be expanded by the use of the immersion probe which can sample pore waters, and the XYZ positioner. The immersion probe is being tested on two August 2002 cruises, and the XYZ positioner should be completed by early 2003.

- In 2003 we plan to use the LRS to make measurements of gas vents and hydrates in the Gulf of California on the R/V Western Flyer (Brewer, et al., in press). Prior experience has shown that gas collected from sea-floor vents often forms hydrates in the sampling equipment potentially altering its composition. *In situ* LRS will allow us to determine the gas composition without this potentially artifact-inducing complication.

- Laser Raman spectroscopy is capable of discerning minerals prevalent at hydrothermal vent systems both in chimneys and as precipitates in the vent plume (e.g., anhydrite, sphalerite and pyrite — Pasteris, 1998). The increased sensitivity provided by liquid core optical fibers (LCOF) should also allow measurements to be made of dissolved species in vent fluids (e.g., CO_2, CH_4, and H_2S). We propose to visit northern high-temperature hydrothermal vents (e.g., Cleft) in 2004 with the Western Flyer (two dive days will be needed). Discussions with D. Stakes (MBARI), D. Kelley (Univ. of Washington), and J. Pasteris (Washington University) have shown that there is great interest in using laser Raman techniques for studies of mineralogy and chemistry in vent environments.

- Sites within Monterey Bay (accessible via the R/V Point Lobos) are also of interest. Bacterial mats from Monterey Bay (collected by Ventana) have been studied in the lab with Raman spectroscopy by MBARI researchers with colleagues from Washington University (Pasteris et al., 2001). We would like to attempt similar experiments *in situ*. Also, the immersion probe can be used to analyze sediment pore waters around seep communities in Monterey Bay.

- In order to improve our understanding of laser Raman spectroscopy, and to elucidate measurements made at sea, it is necessary to perform a series of laboratory measurements. Lab work will help us to prepare for measurements made in new environments, and to clarify the results and allow proper interpretation of the spectra obtained in the field. D. Stakes will provide fresh chimney samples for analysis. J. Pasteris has already provided a number of mineral standards for laboratory measurements. Lab work is currently being performed (in conjunction with colleagues at Washington University) to better understand the spectra of seawater which is the background for all of our measurements. Solution speciation can be detected by Raman spectroscopy but sophisticated approaches are necessary. Laboratory testing is also necessary to develop methods for using LCOF and silver SERS.

References

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Pasteris, J. D., J. J. Freeman, S. K. Goffredi, and K. R. Buck, Raman spectroscopic and laser scanning confocal microscopic analysis of sulfur in living sulfur-precipitating marine bacteria, Chem. Geol. 180, 3-18, 2001.

Wang, A., L. A. Haskins, and E. Cortez, Prototype Raman spectroscopic sensor for *in situ* mineral characterization on planetary surfaces, Appl. Spectrosc. 52(4), 477-487, 1998.

c) Specific deliverables (new and continuing projects)

- An improved, high-quality LRS will be delivered to Science

- A “Through-the-lens” visualization system will be implemented
- A laser shutter will be installed
- LCOFs will be integrated with the probe head for increased sensitivity
- New fiber optic cables will be acquired and installed

d) Project team (new and continuing projects)

Science related tasks: Peter Brewer, Edward T. Peltzer, and Sheri N. White

Engineering related tasks: Mark Brown (ME), Danelle Cline (SE), TBD (EE), and Sheri N. White

e) Project Lab Space (new and continuing projects)

An enclosed area (i.e., without windows to hallways or outside) for lab use of the LRS will provide the dark environment needed for laboratory studies and will protect users and passers-by from stray laser light. Because much of the lab work will require fluids, proximity to plumbing is preferable. Bench space is required for removing the instrument from the pressure cases for maintenance and engineering enhancement work.

3) Budget Justification (new and continuing projects)

The following Capital Expense items will be purchased (MBARI does not have the capability to produce them in-house) during 2004:

1) Through-the-lens (TTL) visualization system from Kaiser Optical Systems, Inc. -- $12,000.
2) Small pressure vessel for the LRS optical probe head (larger than the current pressure case to contain the TTL system) -- $10,000

Less expensive items such as laser shutter components, titanium for custom end caps (for use with the immersion probe), sample cells, and standards are included in Engineering and Science Lab Supplies ($7500 each). We have requested $2000 in General Supplies based on previous experience.

A new laptop computer and appropriate software is requested at a total cost of $3500. This will increase the portability of the LRS system, which is useful for a seagoing instrument (and necessary if the instrument is to be reduced in size for use on submersibles). Current-generation laptops are as good or better than the current, bulky LRS desktop computer.

A visit to Kaiser Optical Systems, Inc. in Ann Arbor, MI will allow us to work with the vendor to adapt a standard, microscope, TTL system to our LRS (which has unique limitations such as space, power/communications, etc.). $10,000 of Outside Services is requested to have Kaiser customize the TTL hardware and software (they provided customization services for the spectrometer control software in Phase I).

Visits with our colleagues at Washington University in St. Louis, MO are necessary for developing spectrographic techniques for the new methods we hope to employ (i.e., LCOF and SERS) and the new targets we hope to analyze (e.g., hydrothermal vents). They currently have a Kaiser spectrometer with a TTL system and can offer insight in the development and use of the MBARI TTL system. Conference fees and travel, and publication fees are need to communicate our advances and findings to the larger scientific community.

4) Milestones (new and continuing projects)

	XYZ Precision Positioner	TTL Visualization	Laser shutter	Documentation	**Total Resources** [1] for each resource category for all milestones listed here
Milestone date	04/01/03	12/31/03	03/30/03	12/31/03	
Milestone description	Complete integration and testing	Working system & new pressure case	Working system	Paper work done	
EE	10	30	20	5	65
SE	15	20	20	5	60
ME	15	30	20	5	70
IAG					
Machine Shop		20	10		30
ME Tech		10	10		20
EE Tech		5	5		10
DMO/ROV pilots	5	5			10
ITD				20	20

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