Annual Report

Development and deployment of a modular, autonomous *in situ* underwater stable isotope analyzer

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LONG-TERM GOALS

The long term goal of this project is the development of a reliable and robust submersible instrument capable of *in situ* carbon stable isotope measurements of dissolved methane and carbon dioxide.

OBJECTIVES

The technological objectives for the development of this instrument involve 1) the instrument reconfiguration into a package compatible with deep sea pressure housing 2) a high pressure membrane inlet allowing extraction of analyte gases at depths of up to 4000m 3) calibration and standardization of the instrument 4) and the development of a waste gas removal system.

APPROACH AND WORK PLAN

1. The development of the deep sea ICOS stable isotope analyzer is moving forward on two fronts: engineering and calibration. The engineering approach has involved reconfiguration of a commercially available bench-top ICOS instrument to operate in a cylindrical pressure housing as well as the design of a membrane inlet and gas handling system for transferring analyte gases into the laser cavity for measurement. Both of these tasks have been largely accomplished. The calibration approach has involved a lab-based high pressure flow-through calibration membrane inlet. Concentrations of both methane and carbon dioxide from calibration fluids are analyzed independently on an independent gas chromatography system which is calibrated regularly with gas standards. Stable isotopic measurements of calibration fluids will be calibrated using discrete samples taken and analyzed at a commercial isotope facility.

2. Key individuals working on this project include:
   - **<u>Dr. Scott Wankel</u>** – Postdoctoral Research Scientist at Harvard – responsible for calibration efforts and lead scientist for all field deployments including interfacing the instrument with ROV, cabled observatories and other deep sea applications. Dr. Wankel and Dr. Girguis will also lead data collection and interpretation.
   - **<u>Dr. Manish Gupta</u>** – Senior Project Engineer – responsible for overall instrument design engineering and fabrication.

- **<u>Dr. Robert Provencal</u>** – Senior Project Scientist – responsible for ICOS instrument optics and laser design and testing, oversees electrical and software components.
- **<u>Vimal Parsotam</u>** – Electrical Engineer – responsible for instrument communications and electrical component installation and testing.

3. **Work Plans:** The upcoming year (December 2008 through December 2009) affords this project several prime opportunities to complete dive missions with the ICOS instrument visiting both hydrocarbon cold seeps as well as high temperature hydrothermal vents. The first upcoming expedition is a repeat cruise with two dives (*ROV Ventana*) to the Monterey Canyon methane cold seeps that were visited in October 2008. The completion of these two dives should represent the completion of the first phase of the instrument engineering and proof-of-concept. The period from January 2009 through April 2009 will represent a time of more intense calibration and characterization of the instrument performance (of both CH_4 and CO_2 concentration and isotopic composition) at the Girguis lab at Harvard using a high pressure inlet and calibration system. In May 2009, there will be one dive (*ROV Ventana*) again to the cold seeps found in Monterey Canyon, during which we will begin testing the instrument's capability for simultaneous measurement of both CH_4 and CO_2 stable isotope and concentrations. This will be the first dive of the second phase of the development and will represent the first ever *in situ* co-registered measurement of $\delta^{13}C$-CO_2 and $\delta^{13}C$-CH_4. Later, in July 2009, the instrument will be deployed on the *DSV Alvin* – to the hydrothermal vent field along the Juan de Fuca Ridge making the first *in situ* co-registered measurements of $\delta^{13}C$-CO_2 and $\delta^{13}C$-CH_4 of direct hydrothermal vent fluid. Finally, in October of 2009 there will be a return visit to Monterey Bay for a 3-month test deployment and interfacing with the MARS deep sea observatory cable.

WORK COMPLETED

At this time the project team has completed the redesigning and repackaging of the ICOS instrument to fit into a titanium pressure housing. The instrument now measures approximately 44 inches in length, with a diameter of approximately 7 inches. Furthermore, the design includes improved electronic controls for the solenoid valves and extended battery life to >6 hours. Additionally, the instrument can now be powered by external ROV/DSV/Cable power. Finally, a hardware development has lead to improved data acquisition, such that two lasers can be 'duplexed' and thus, two analyte gases simultaneously analyzed. This represents a major improvement, streamlining the development of a 'multi-gas' analyzer.

We have also completed one fully successful dive with the ROV *Ventana* on October 6th, 2008, during which we successfully operated the instrument to a depth of 970m while sampling small methane cold seeps in the Monterey Canyon, CA. This mission established the successful design of the instrument electronics and communications. As expected, this mission also shed light on areas in need of improvement such as the internal gas handling system (leaky solenoid valves, inappropriate chamber volumes, etc.). Primarily, it was believed that the extraction of sample gas into the laser cavity was insufficient to provide enough sample gas for analysis in the water column, where methane concentrations are expected to be quite low. Currently these issues are being re-engineered for two upcoming dives in mid December (12/18 and 12/19) to the same location.

RESULTS

We were very pleased with the success of our first deployment, which was quite significant, as it represented the ***first successful operation of a fully submersible ICOS (integrated cavity optical spectroscopy) instrument***. Ethernet communications were established for monitoring the instrument's performance in real time and maintained from the surface to the full depth of 970m. During this deployment the instrument was powered on internal batteries, which also provided proof of the capability of future 'cable-free' autonomous operation. In conclusion, at the end of only three months of project funding we have successfully demonstrated a fully operational engineering design, capable of real-time *in situ* data analysis on short time-frame deployments.

IMPACT AND APPLICATIONS

Economic Development

To date, the ICOS technology has been used to measure a wide variety of compounds in laboratory "benchtop" systems. The development of a deep sea instrument, which can easily be downgraded for use in less challenging environments, brings the ICOS technology to the environmental sensor market. Thus, this effort should directly stimulate economic development of the this market, including, for example, governmental environmental quality monitoring (EPA, USGS, etc.), small municipalities interested in efficient monitoring of drinking water supply quality, and/or watershed pollution prevention agencies. Furthermore, specifically as an advanced tool for natural gas exploration (e.g., methane), this technology could indirectly stimulate a market centered around more efficient natural gas exploration and characterization.

Quality of Life

This sensor technology could be used in a wide variety of water quality monitoring applications, such as tracking the inclusion of natural gas into municipal water systems or supervision of protected or endangered natural resources such as estuaries. The development of this instrument, and others like it, are critical in enabling us to better monitor and assess environmental changes in real time, including water quality impacts and natural variations of ecological relevant compounds, such as methane and carbon dioxide.

Science Education and Communication

The Girguis lab is heavily involved in education and outreach. Peter Girguis is a part of the Howard Hughes Medical Institute Undergraduate Research Fellowship (HHMIUF) program. Girguis currently has undergraduates – all minority and high risk students-- working in the laboratory under his supervision. In addition, Peter is working with the Cambridge Rindge Latin School, a local public high school, to allow students from disadvantaged backgrounds the opportunity to work in a Harvard research laboratory. Peter Girguis is also working with the Gulf of Maine Research Institute to develop the world's first deep-sea hydrocarbon seep exhibit. This exhibit is designed to illustrate how methane supports unique and diverse ecosystems around the world. This exhibit would be viewed by thousands of students and adults who visit the GMRI through their New England Marine Science program, as well as their summer public lecture series. Ed Seidel, a foremost authority in aquarium design (and formerly a project leader of the deep sea exhibit at the Monterey Bay Aquarium) is currently at the GMRI and will work with us to bring this exhibit to fruition.

Figure 1. First field deployment of the in situ ICOS instrument on the *ROV Ventana* aboard the R/V Point Lobos on October 6th, 2008. The instrument is housed inside a cylindrical titanium pressure housing positioned in the rear of the ROV (orange circle). The sampling wand, through which sample fluids are delivered to the membrane inlet on the housing, is in the port manipulator (blue circle).