Annual Report - 2009

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 include 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 currently 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:

- **Dr. Scott Wankel** – Lead 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 will also play the role of lead scientist for the purposes of data collection and interpretation.
- **Dr. Manish Gupta** – Senior Project Engineer – responsible for overall instrument design engineering and fabrication.
- **Dr. Robert Provencal** – Senior Project Scientist – responsible for ICOS instrument optics and laser design and testing, oversees electrical and software components.
- **Vimal Parsotam** – Electrical Engineer – responsible for instrument communications and electrical component installation and testing.

3. **Work Plans**

The coming year (October 2009 through October 2010) presents several exciting deployment opportunities for the ICOS instrument again including a variety of geochemically contrasting deep-sea environments. Phase I ('Proof of concept') has been largely accomplished and we are now dealing with tasks such as dynamic calibrations (*in situ*) as well as a more complete characterization of potential stable isotopic fractionation effects (and the potential for influence on analytical precision and accuracy) inherent in the *in situ* ICOS system in its current configuration. This characterization will be carried out at Harvard using the high-pressure benchtop calibration sample inlet attached to the ICOS instrument.

Future deployments will include environments such as a hydrocarbon cold seep (Monterey Bay), a hydrocarbon rich brine pool (Gulf of Mexico) and a high temperature hydrothermal vent system (Juan de Fuca Ridge). These diverse environments will allow us to more completely evaluate the response of the instrument under conditions widely varying in physical parameters such as salinity and temperature. In November of 2009, we will return to Monterey Bay continuing with our spatial characterization of the cold seep environments previously visited in our 2008/09 deployments. In addition to fine-tuning our operations, we aim to ground-truth of our *in situ* methane concentration and stable isotopic composition measurements by analyzing pre-calibrated solutions sampled directly during deployment. In addition to the regular analysis of internal gas standards during deployment (for evaluating instrument drift), this 'procedural standard' will allow further evaluation of any potential fractionation effects encountered during the transfer of dissolved gas from the environment into the analytical cell.

Deployment at sites such as the Gulf of Mexico brine pool and Juan de Fuca hydrothermal vent system represent efforts to demonstrate the broad capability of the instrument during operation in a variety of deep sea environments (e.g., high salinity brines and high temperature vent fluids).

WORK COMPLETED

Since last report have completed two successful deployments in Monterey Canyon.

1. December 2008. During deployment in December 2008 we made the first successful in situ measurement of deep-sea methane stable isotopic composition. Several design characteristics were tested during this deployment, such as… We were able to establish a lower limit of detection for acceptable $\delta^{13}C$ CH_4 composition (~17mM), which allowed for $\delta^{13}C$ precision of ± 6‰ (Figure 1). This level of precision, of course, is less than our goal (1‰), however, represents an important step forward.

This deployment shed light on a number of areas for potential improvement (e.g., vacuum problems due to H_2S and vapor in sample fluids – corrosive to solenoid valve seats). As such, an entirely new instrument was redesigned and engineered for deployments beginning in the summer of 2009. These improvements included:

- New solenoid valves with PEEK seats, which will reduce problems caused by corrosion of metal parts exposed to gases containing high H_2S and water vapor.
- Smaller vacuum pump (two head vs four head), which achieves the same vacuum in less space and using less power
- New laser cell (22cm), longer and wider mirrors, which increases sensitivity

- New software control system (based in LabView), which increases modularity and ease of use
- Independent ethernet control interface (IP-KVM), which allows for remote access

2. August 2009. During deployment in August 2009 we were able to successfully ‘map’ methane stable isotopic composition over a ‘fine scale’ resolution of a cold seep (~2m). Several measurements were made including fluid directly from the seep orifice as well as ‘pore fluids’ sampled immediately after push cores were taken through seep sediments. This project resulted at least 4 different measurements of methane concentration and carbon isotopic composition and represents a major achievement for the development of *in situ* geochemical sensors (manuscript in preparation).

Also during this deployment we were able to monitor instrument drift by way of periodic measurement of an internal sample of standard methane (-46.7‰). Average values measured for the standard were 44.5‰ with a standard deviation of 1.2‰.

August 12, 2009 Dive. Observed dramatically increased sensitivity. Extensively sampled two different sites. While we are establishing the lower limits of our sensitivity, we have chosen not to focus on deployment to the hydrothermal vents at Juan de Fuca this year. Instead, we are focusing on establishing the accuracy of the instruments in more methane-rich sites such as Monterey Bay, the Gulf of Mexico, and Hydrate Ridge. Also, to facilitate longer duration times, the instrument runs off of 120VAC power; an inverter can be placed internally if DC power is supplied from the platform. Internal batteries have been removed. Our long-term goal is to make these units modular and interchangeable, which can be easily accomplished.

RESULTS

We were extremely pleased with the success of the past year’s accomplishments, which included the ***first and second successful in situ measurement of methane concentration and carbon isotopic composition using a fully submersible ICOS instrument.*** The newly engineered instrument improved our analytical sensitivity by at least a factor of 4.

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. We plan on including this instrument (or a mockup) as part of a SCIENCE AND TECHNOLOGY Forum, illustrating to schoolchildren how advances in the tech sector can positively influence our ability o conuct cutting edge science.

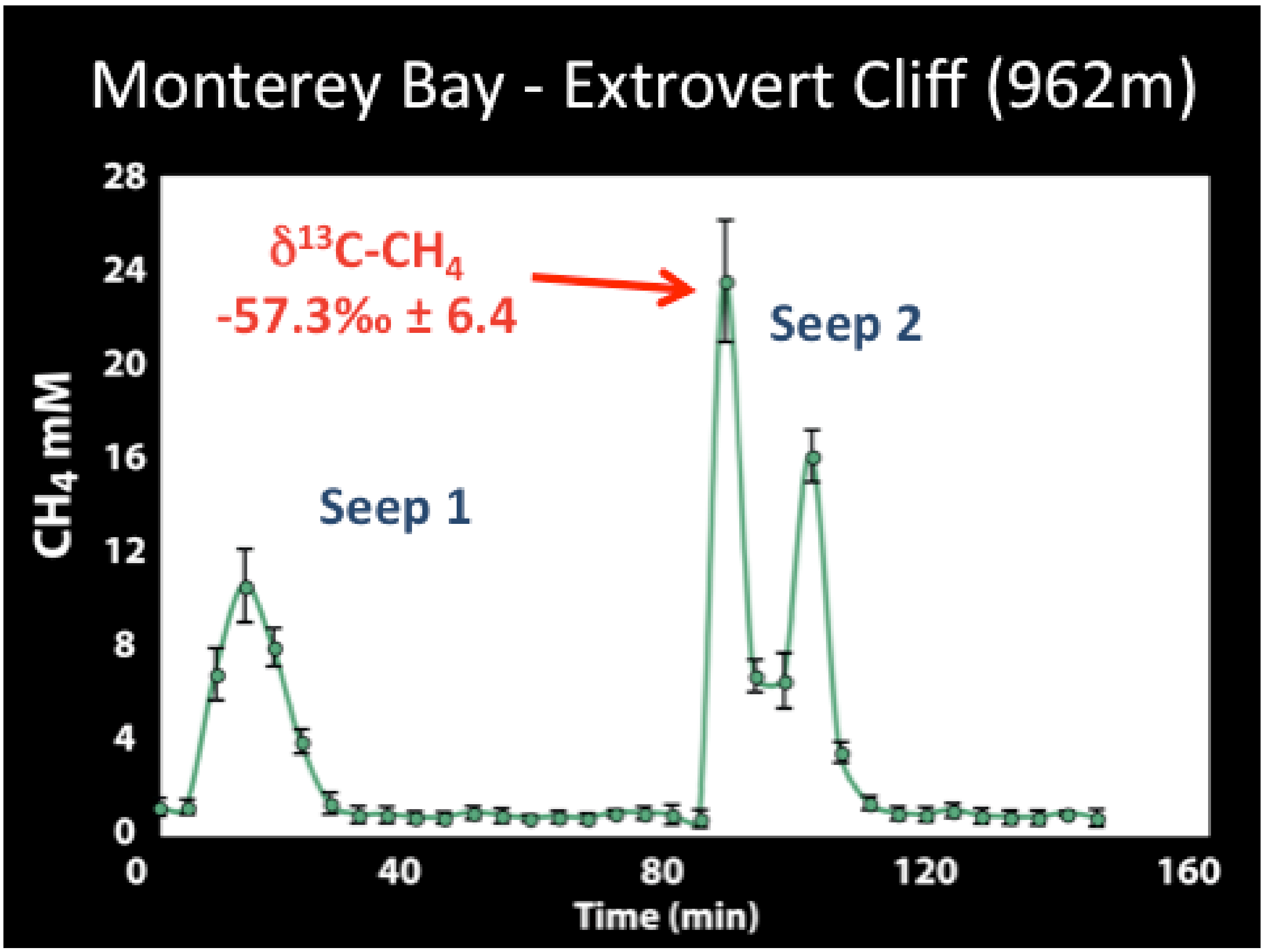

Figure 1. First successful in situ measurements of methane concentration and stable isotopic composition made on the ROV Ventana aboard the R/V Point Lobos on December 19th, 2008. Two seep sites were visited over the course of the 2.5 hour long dive during which fluids were sampled continuously through the sampling wand. In this previous instrument configuration, accurate stable isotopic composition was limited to samples above ~17mM. A value of -57‰ was measured and agrees reasonable well with previous samples collected from this region by others and analyzed by conventional lab based isotope ratio mass spectrometry.