<u>Annual Report</u>

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 previous years (2008 through December 2009) afforded 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 expedition was a cruise (on the *RV Point Lobos* and using the *ROV Ventana*) to the Monterey Canyon methane cold seeps in October 2008, followed by two other dives to the same field site in 2009. These two dives represent the completion of the first phase of the instrument engineering and proof-of-concept, and the data recovered demonstrate the efficacy of this instrument (see below). January 2009 through April 2009 was 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, was 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 was first dive of the second phase of the development and will represent the first ever *in situ* co-registered measurement of $\delta^{13}C\text{-}CO_2$ and $\delta^{13}C\text{-}CH_4$. Finally, in October of 2009 there was a return visit to Monterey Bay for a 3-month test deployment and interfacing with the MARS deep sea observatory cable. Finally, we are taking advantage of recent events in the Gulf to demonstrate the efficacy of this technology. In Spring of 2011, we will be deploying this instrument in the Gulf of Mexico, near the site of the BO oil spill, as well as naturally occurring oil seeps and brine pools, to isotopically "map" the methane from the oil spill, and to better understand stable carbon isotope dynamics in naturally occurring seeps.

WORK COMPLETED

As previously mentioned, the project team has completed the redesigning and repackaging of the ICOS instrument to fit into a titanium pressure housing. The instrument 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 three fully successful dives with the ROV *Ventana* 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.

RESULTS

To better explain the value of the results we have provided a brief introduction into anaerobic methane oxidation (or AOM). AOM plays an important role in global climate change by governing the release of methane from anoxic sediments into the global ocean and ultimately the atmosphere. Thus, gaining an accurate understanding of both the distribution of methane sources and the occurrence of AOM as well as the spatial and temporal variability of cycling pathways is critical. Environmental analyses of methane stable isotopic composition ($\delta^{13}C_{CH4}$) provide just such an indicator of methane source, whether biogenic or thermogenic, as well as a spatial and temporal integrator of microbial cycling pathways, such as AOM. Our newly developed *in situ* methane stable isotope analyzer -the primary focus of this project- is capable of measuring $\delta^{13}C_{CH4}$ to full ocean depths. The instrument had an operating wavelength of 1647 nm and used chemometric spectral decomposition to determine the relative concentrations of $^{13}CH_4$ and $^{12}CH_4$ with a sensitivity of ± 0.2‰. Deployments to cold seep environments revealed a distinct separation in carbon isotopic composition between methane in advecting fluids as compared with methane from sediment pore fluids. During multiple visits to two different sites at Extrovert Cliff in Monterey Bay (960m), methane in advecting fluids ranged from -70.2‰ to -63.8‰. In contrast, methane-rich fluids sampled directly from pushcore holes taken through seep sediments contained methane with substantially higher $\delta^{13}C$ values ranging from -64.2‰ to -50.2‰. These data implicate the influence of anaerobic oxidation of methane within these seep sediments. While the advective flux of methane to the seafloor from the central orifice of the seep is substantial, using conservative values for the fractionation factor of AOM (ε = -24‰), we estimate that a minimum of 57 to 70% of the diffusive flux of methane through seep sediments is consumed by AOM.

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, including HIGH PRECISION oil spill monitoring. With the isotope ratios and concentrations of methane, one can much better pinpoint the source of methane. Also, this technology facilitates the 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.

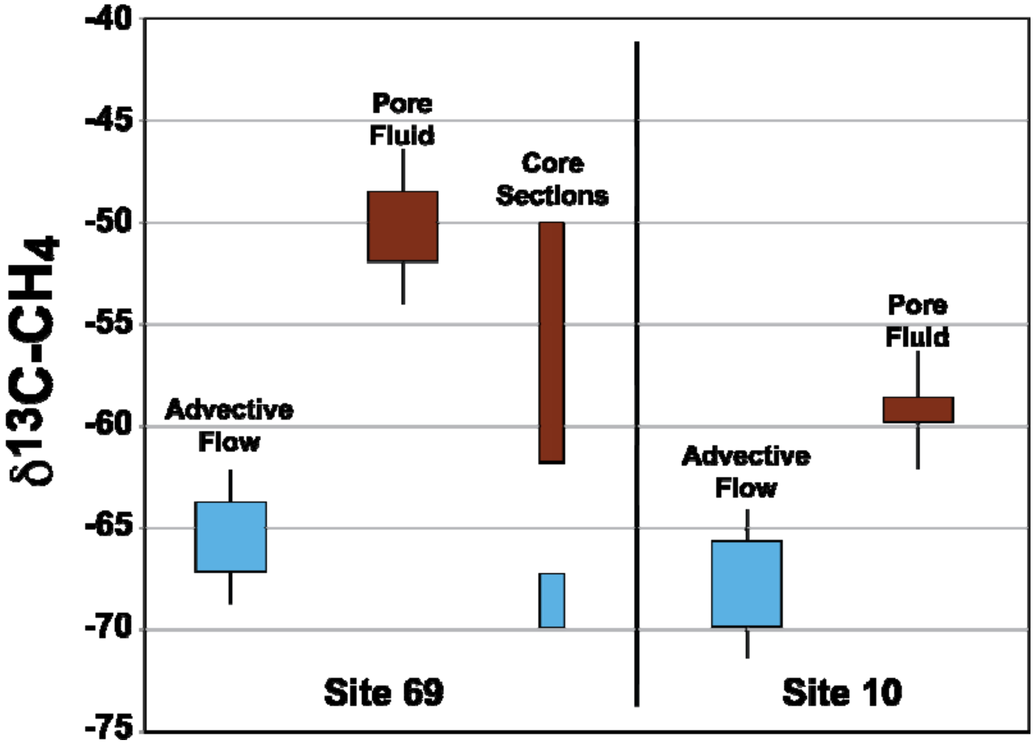

Figure 1. At a site known as Extrovert Cliff in the Monterey Canyon (960m), methane is extracted from seep fluids and rapidly analyzed for concentration and stable isotopic composition. Core hole and advective fluids exhibit distinctive isotopic compositions, which indicates both the source fluid and rate of methane oxidation. Obtaining such information in real time fundamentally changes our understanding of biogeochemical processes, by affording much higher spatial resolution that generates better models of processes.