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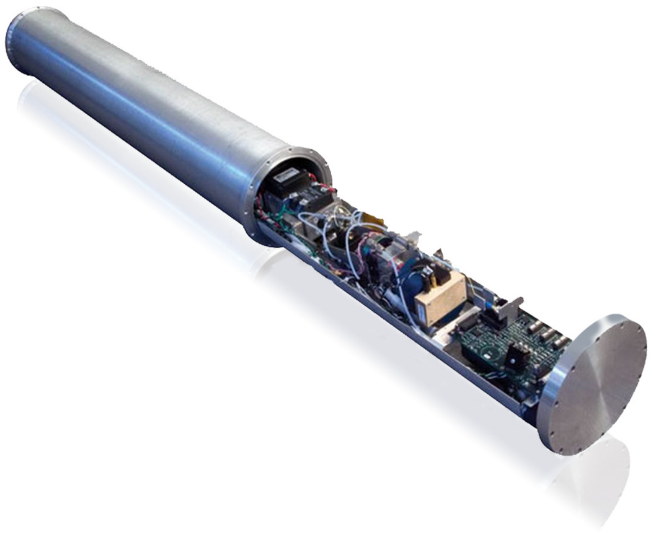
Studying methane sources and cycling in deep sea environments

Los Gatos Research (LGR)

Marine sediments represent the largest single source capable of producing methane, an important greenhouse gas. Geochemical and microbiological studies have shown the importance of anaerobic oxidation of methane (AOM) by microbes as a primary regulator of sedimentary methane flux to the ocean and atmosphere.

Measurement made easy



Problem

The precise nature of AOM continues to be uncertain and remains a subject of intense research.

The study of the marine methane cycle becomes difficult in the deep ocean. When recovering sediments from the deep ocean, samplers that don't retain pressure generally suffer from outgassing caused by depressurization, making interpretation difficult. Pressure-retaining samplers typically target limited collection from prominent features such as hydrothermal vents and are impractical for broad spatial characterization of deep ocean environments.

Recent advances in underwater mass spectrometry and other analytical instruments have overcome many of the challenges of quantifying the on-site chemical composition of dissolved volatiles. However, chemical composition alone offers a limited perspective on the underlying processes responsible for the observations. It reflects only the net effect of these processes, not about rates of transformations, types of processes, and magnitude of fluxes.

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Solution

Stable isotope ratios offer a more robust means of disentangling the effects of multiple processes. These ratios can reveal the nature and relative contributions of the biological, chemical, and physical phenomena underlying an observed concentration. Stable isotope analysis has become an invaluable tool across all types of environments, including spatial and temporal scales.

While isotope ratio mass spectrometry (IRMS) serves as the gold-standard method for isotopic analyses, its associated infrastructure precludes field use. Recent techniques in isotope analyzers employing laser absorption spectroscopy have proved to be practical alternatives to IRMS in many applications. In particular, researchers have developed a deep-sea in situ analyzer based on off-axis integrated cavity output spectroscopy (OA-ICOS), a technology patented by Los Gatos Research (LGR), a member of the ABB Group. This analyzer can measure stable carbon isotope ratios of methane (^{13}C:^{12}C) in near real-time at water depths up to 3000 meters.

Fig. 1 shows the layout and major systems of the in situ ICOS analyzer developed for deep sea analysis. The cavity consists of a 28-cm long, 5-cm diameter cell bounded by two highly reflective mirrors (reflectivity = 99.9929%). The cell includes a pressure gauge and thermistor to provide accurate readings of gas pressure and temperature. A distributed feedback diode laser operating near 1648 nm enters the cavity. Laser light from the cavity focuses on an amplified InGaAs detector whose signal is digitized, analyzed, and stored by an onboard computer.

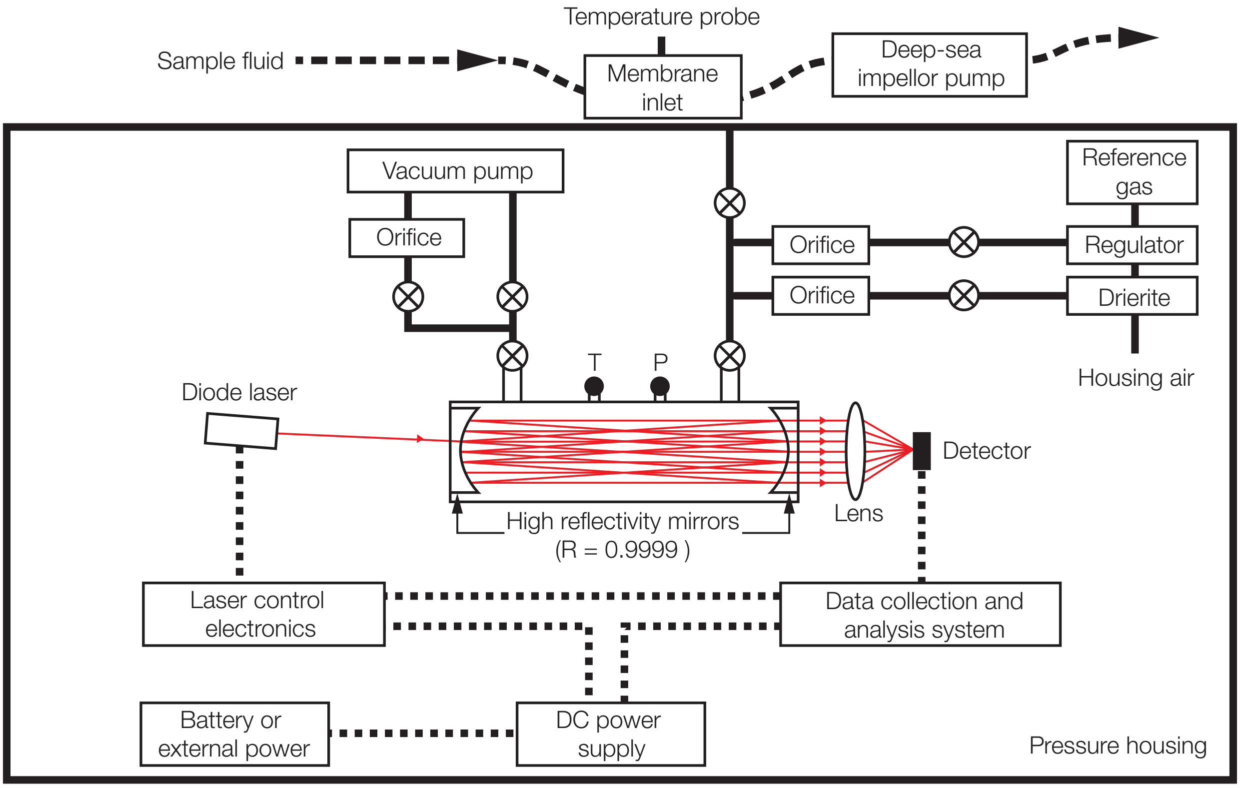

Fig. 1: Layout and major systems of the in situ ICOS analyzer developed for deep sea analysis

The laser is tuned via current to more than 2 cm^{-1} (60 GHz). The system averages the transmission spectra to provide a single spectrum stored for later analysis. Net data rate is 1 Hz. A chemometric data analysis routine processes the acquired spectra. The measurement consists of 97 such analyses to yield a single $\delta^{13}C_{CH4}$ value.

Although based on a conventional ICOS analysis platform from LGR, the researchers reconfigured the instrument as follows:

- to fit into a cylindrical pressure housing capable of surviving at depths of >3000 meters
- to extract dissolved sample gases through a membrane inlet
- to deliver extracted gas into the analytical cell
- to compare analyses to onboard isotope reference standards

For sampling, a pump continuously runs seawater through the inlet at flow rates ranging from 50 to 250 mL/min. A customized gas handling system transfers sample and reference gases within the instrument and controls vacuum pressure within the measurement cell.

The system independently references the measured carbon ^{13}C:^{12}C for each sample to a periodic internal analysis of known reference gas. This permits correction for any drift due to changes in electronic gain or sensitivity, or to ambient conditions. Between each reference and sample analysis, the ICOS cell and transfer lines are purged with dry air or N_2 to eliminate carryover between sample and reference analyses.

The system expresses the measured transmission spectrum as the sum of a baseline and absorptions due to $^{12}CH_4$ and $^{13}CH_4$. The result of the analysis and fitting techniques provides absolute concentrations of $^{12}CH_4$ and $^{13}CH_4$ (ppmv) and are used to calculate both methane concentration in the cell and carbon isotope ratio ($\delta^{13}C_{CH4}$) expressed in permil (‰). Lab experiments have characterized and validated the instrument's analytical capabilities and performance.

Results

Researchers conducted two deployments of the reconfigured in situ ICOS analyzer to methane seeps in Monterey Bay at a site called Extrovert Cliff. Water depth was about 962 meters. These studies have provided the first in situ stable isotope-based characterization of how anaerobic methane oxidation affects methane flux from seep sediments. The data gathered demonstrate the efficacy of the analyzer as an effective platform for the analysis of $\delta^{13}C_{CH4}$ within deep-sea environments, and consequently across a wide range of applications. For example, monitoring of changes in $\delta^{13}C_{CH4}$ could provide a more sensitive means for early detection of important changes in subsurface tectonic activity to predict earthquakes and eruptions.

Current development efforts are aimed at improving performance through the removal of water vapor to increase the proportional concentration of methane in the ICOS cell. Using a more powerful laser, a longer path length, and a heated optical cell should also lead to improved sensitivity. These improvements along with perfection of the fluid sampling system will permit finer-scale analyses of variations in AOM activity. They will also facilitate advances in using $\delta^{13}C_{CH4}$ and other isotopic systems to interrogate bio-geochemical cycles in the deep sea and other remote or challenging environments.

References

Information based on 'Characterizing the Distribution of Methane Sources and Cycling in the Deep Sea via in Situ Stable Isotope Analysis,' Scott D. Wankel et al, *Environmental Science & Technology*, 2013, 47 (3), pp 1478-1486.

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