Techniques for Analyzing Dissolved Gases in Seawater

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Laser Raman Spectroscopy

Advancements in the development of deep submergence platforms such as remotely operated vehicles (ROVs) and autonomous underwater vehicles (AUVs) are giving scientists greater access to the deep ocean. Likewise, seafloor observatories provide newly emerging opportunities to monitor seafloor environments over sustained time periods. These technologies are enabling ocean scientists to move away from mere *sampling* (bringing back samples from the deep ocean for analysis in the lab) toward *sensing* (measuring actual processes in real-time on the seafloor).

Hydrothermal vent systems are the subject of a great deal of interdisciplinary research and a key topic for the DOEI. A variety of dynamic processes occur at these sites that support life and influence ocean chemistry and seafloor geology. Located on seafloor spreading centers, rising magma at vent sites heats and alters seawater percolating through the ocean crust. The hydrothermal fluid emerging from the seafloor is super hot and contains high concentrations of metals and dissolved gases. Some of these are greenhouse gases, such as carbon dioxide (CO_2), methane (CH_4) and hydrogen sulfide (H_2S).

Currently, scientists study these fluids by collecting samples in gas-tight bottles and returning them to the surface for analysis in the laboratory. However, new technologies are being developed that will allow hydrothermal fluids to be analyzed *in situ* – on location. These techniques include *in situ* mass spectrometry (like instruments being developed by Rich Camilli; see the 2006 DOEI annual report) and laser Raman spectroscopy, which I employ.

Laser Raman spectroscopy is a non-invasive, non-destructive technique that can identify a range of solids, liquids and gases. It is a useful tool in a variety of fields, including medicine, pharmacology, materials science, biochemistry and geochemistry. It can be used to identify drugs and explosives and for various types of industrial process monitoring. Because it is rapid and requires no sample preparation, laser Raman spectroscopy is well suited for *in situ* oceanographic analyses. A number of oceanic targets of interest can be analyzed by this technique, including the dissolved gases and minerals (sulfides and sulfates) released from hydrothermal vents.

In this technique, a laser is used to "excite" a sample at the molecular level. The back-scattered light from the illuminated spot is collected with a lens and sent to a spectrometer, where the intensity at various wavelengths is recorded. Most of the light is elastically, or "Rayleigh" scattered – that is, light is scattered back at the same wavelength as the incident light. However, a small amount is inelastically, or "Raman" scattered – the light is shifted in wavelength due to its interaction with the molecule. The shift in wavelength (or energy) is equal to the vibrational energy of the molecule. So, the Raman spectrum serves as a "fingerprint" of a molecule by providing chemical and structural information about the molecule.

Many of the gases in hydrothermal fluids are Raman-active, such as CO_2, CH_4 and H_2S. DOEI support is allowing me to perform laboratory experiments with these dissolved gases to determine calibration curves for the chemicals in seawater. The methods ironed out during this project will allow future development of a new sea-going Raman system that is optimized for the real-time *in situ* analysis of dissolved gases in the deep ocean. These instruments will be deployed on AUVs, ROVs and at seafloor observatories. Using these instruments, scientists will be able to better elucidate the concentration of these chemicals around vent sites and the relative sources and sinks for greenhouse gases in the ocean.