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Laser Raman Spectroscopy Used to Study the Ocean at 3600-m Depth

Making geochemical measurements in the deep ocean is fundamentally difficult. For this reason, century-old technologies using water bottles and cores for sample recovery still provide the basic tools. With the development of research submersibles and remotely operated vehicles (ROVs), however, new opportunities for sophisticated sampling and analysis have arisen.

A laser Raman spectrometer has been deployed for the first time in situ to study deep ocean science. Raman spectroscopy has its origins in ocean science, for it was the "wonderful blue opalescence of the Mediterranean Sea" that first stimulated C.V. Raman to investigate the molecular scattering of light [*Raman*, 1930]. Many laboratory results of laser-excited Raman spectroscopy are applicable to deep ocean research. The identification and characterization of minerals, the speciation of dissolved complexes and gases, chemical-structural characterization of gas hydrates [*Sum et al.*, 1997], and sulfur speciation in filamentous benthic bacteria [*Pasteris et al.*, 2001] provide important examples. The latter two represent especially important ocean geochemical targets that are best studied in situ.

The instrument we adapted is a Kaiser Optical Systems spectrometer with a transmissive holographic grating and a Charge-Coupled Device (CCD) array detector. The exciting laser is a 532-nm, frequency-doubled Nd:YAG laser yielding ~30 mW at the probe head. The instrument was housed in three pressure cases for ocean deployment: one held the laser and a single-board computer, a second the spectrometer and CCD detector, and the third held the optical probe head (Figure 1) that both projected the laser beam and captured the back-scattered Raman radiation.

The system, which was placed on the ROV *Tiburon* [*Brewer et al.*, 1999], was deployed on four successful dives to a maximum of 3610 m depth. The spectrometer and laser housings remained on the ROV tool sled, while the probe head—which was connected by fiber-optic cable—was manipulated by the robotic arm to bring the laser into focus on the sample (Figure 1). The instrument was controlled from the surface ship using the Kaiser HoloGRAMS software over an ethernet link through the vehicle fiber-optic tether. Wavelength-calibration of the spectrometer was done in the laboratory with a neon-emission lamp and on deck and at depth using isopropanol and diamond as standards. The calibration protocols are being refined to quantify depth-related effects on the spectrometer due to both temperature change and pressure-induced deformation of the housing. For measurements made at depth, the accuracy in reported peak position currently is ±3 cm^{-1}, while the precision is ±0.4 cm^{-1}.

Raman spectra of sea water were obtained throughout the water column to characterize both instrument performance and the ocean background medium. In situ spectra of several-centimeter calcite cleavage fragments that were transported to depth were also obtained. We are using the instrument to investigate oceanic sequestration of fossil fuel CO_2 [*Brewer et al.*, 1999]. Spectra were taken of CO_2 injected in situ into an inverted glass beaker at 200 m depth, and changes observed during transit to 664 m. Results show the band shifts associated with changes in the density of CO_2, including the spectrally obvious gas-liquid phase transformation. Liquid CO_2 was also injected at 3600 m depth either directly onto the sea floor (spectrum in Figure 2), into a glass beaker (Figure 1), or into specially designed corrals. The growth of CO_2 clathrate hydrate, the formation of secondary solid and dissolved species, the formation of CO_2-saturated boundary layers, and the dissolution of sea-floor minerals due to the introduction of CO_2 are future targets of Raman investigation.

Hydrothermal vents on the sea floor and their associated bacterial mats are other ideal future candidates for exploiting Raman spectroscopy's ability to characterize solids, liquids, and gases. Both CH_4 and H_2S vent gases are excellent Raman scatterers. Raman spectra provide information on molecular-structural speciation, which can permit the distinction between polymorphs, for example, calcite versus

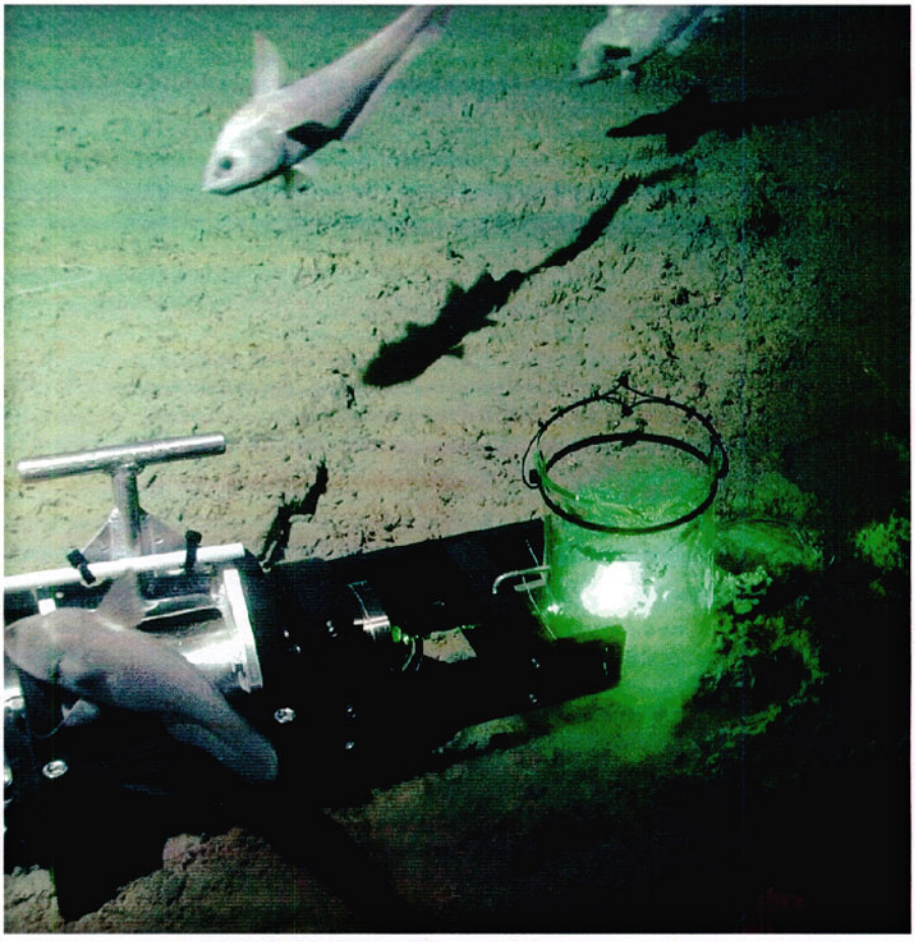

Fig. 1. Shown here is a 532-nm laser beam exiting the Raman probe head, which is in its pressure housing, during spectral acquisition from liquid CO_2 in a 4-l beaker (15.5 cm in diameter) on the sea floor at 3607 m depth, 1.5°C.

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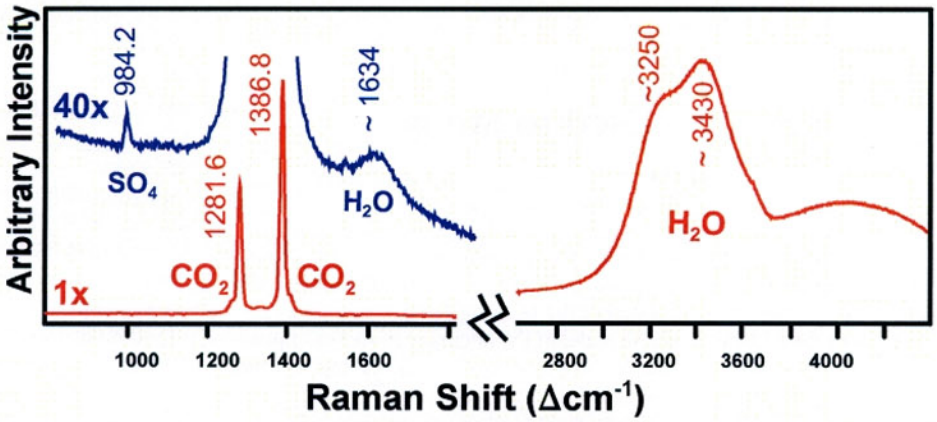

Fig. 2. Raman spectrum of liquid CO_2 placed directly on sea-floor sediments (image not shown). Spectrum shows two strong bands of the Fermi diad for CO_2, as well as the background spectrum of sea water, including the H_2O bend (~1630 Δcm^{-1}), O-H stretch (~3400 Δcm^{-1}), and S-O stretch (~984 Δcm^{-1}; bulk sea water SO_4^{2-} concentration is about 28 mM).

aragonite or wurtzite versus sphalerite. They can also provide inferences about oxidation state and pH in deep ocean environments.

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