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Instruments and Methods

Development and deployment of a deep-sea Raman probe for measurement of pore water geochemistry

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ABSTRACT

We have developed, deployed, and tested a novel probe for study of the geochemistry of sediment pore waters based upon Raman spectroscopy. The Raman technique has already been used successfully for in situ measurements of targets of scientific interest including gas and hydrothermal vents and complex gas hydrates, but sediment geochemistry has so far been an intractable problem since the sediments themselves are strongly fluorescent and typically only very small sample volumes are obtainable. The 35 cm long probe extracts pore fluids through a 10 μm sintered metallic frit and draws the sample through a 2 mm diameter channel into a sapphire windowed optical cell within which the laser beam is focused and the spectrum recorded. The dead volume of the system is ~1 ml and the instrument is ROV deployable with activation of probe insertion and sample withdrawal under direct operator control. The unique features of this mode of detection include observation of the sulfate gradient in marine pore waters as an indicator of diagenesis, direct measurement of the dissolved sulfide species H_2S and HS^-, and measurement of dissolved methane; all of which are of primary geochemical interest. Quantitative analysis is achieved by area ratio to known water peaks and from standard calibration curves with a precision of ± 5%. We find only very small fluorescence from pore waters measured in situ, but observe rapid increases in fluorescence from cores returned to the surface and exposed to oxygen.

1. Introduction

With the development of a deep-ocean laser Raman in situ spectrometer (Brewer et al., 2004; Pasteris et al., 2004); new possibilities arose for non-contact, non-destructive chemical sensing in the deep ocean. Thus far this technique has been applied to gain novel information from field experiments on processes as diverse as the pathways for complex gas hydrate formation (Hester et al., 2006; Hester et al., 2007a), for direct determination of the structure and composition of natural hydrates (Hester et al., 2007b), for observation of mixed gas bubble fractionation processes (White et al., 2006a), and for observations of hydrothermal vent systems (White et al., 2006b).

Raman spectroscopy has traditionally been regarded as a non-quantitative technique due the complexity of the optical path, and thus has typically been used only as a molecular identification tool (Wopenka and Pasteris, 1986). However, while developing controlled ocean CO_2 enrichment experiment techniques, Dunk et al. (2005) demonstrated the ability to make quantitative measurements in the deep sea by using the ratio of the peak areas for target species to the peak areas of known components in the sea water system. The Raman spectra of pure water and sea water are known in great detail with the effects of temperature and salinity being well understood (Walrafen et al., 1986; Furic et al., 2000). Dunk et al. (2005) combined this knowledge with a form of Beers Law to obtain quantitative results in real time from an experiment carried out at 500 m depth. Zhang et al. (2009) extended this technique and obtained novel quantitative laboratory data (± 5%) on the solubility of 1,4-thioxane, a chemical weapons breakdown product, in sea water and demonstrated its ability to form a hydrate in the presence of methane as a help gas.

From the above it is clear that the Raman technique can be applied to the quantitative measurement of those solids, liquids, and gases in the deep sea that have Raman active (polarizable) bonds, but so far the technique has not been applied to sediment geochemistry to gain knowledge of components of the diagenetic process. The reason for this caution is the very strong fluorescence emanating from sea/pore water and deep-sea sediments when

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illuminated by visible light (Coble, 1996); fluorescence is the bane of Raman spectroscopy, frequently overwhelming the relatively weak Raman signal and so strong is this effect that it has deterred investigation.

But much of the geochemical knowledge sought is not from the sediments themselves but from the pore waters that contain the signature of the reactions at work. While fluorescence can occur in some pore waters, there appear to be many instances where this effect is minimal and thus we chose to examine this problem. There are two fundamentally different ways to proceed. The first approach involves laboratory and/or ship-board measurements of conventionally obtained (core/squeezer) pore water samples by focusing the laser beam through the walls of a sealed glass vial, thereby making use of the non-contact, non-destructive capabilities of the Raman technique. This procedure allows technique development and comparison with conventional analyses. In the second approach, pore water measurements are made in situ by inserting the probe directly into the sediments, separating the fluid from the sediment grains and drawing it into a micro-cell, and thus obtaining spectral information directly. We report here on progress made in both approaches.

There have been many techniques applied to study pore water geochemistry, including micro-electrode techniques (Luther et al., 2008), and an array of insertion probes designed to separate the fluid from the host sediments for return to the surface for analysis (Sayles et al., 2001). Raman systems are still large and must be carried and operated by a submersible or ROV to provide power and data return. Nonetheless they do offer some unique sensing possibilities in that the Raman effect can detect important chemical species not easily determined by other sensors.

One example of a unique Raman signal of geochemical importance is the sulfate ion content of marine pore waters in methane-rich sediments. Strong gradients in dissolved sulfate with depth are frequently observed due to anaerobic methane oxidation. Borowski et al. (1996) have convincingly linked the slope of the pore water sulfate signal as a predictor of the depth of the methane gas horizon. The symmetrical sulfate ion is present initially in high concentration in sea water; it has a very strong and well-known Raman signal (Brewer et al., 2004) and is not detectable by any other known in situ technique.

A second example is the detection of dissolved methane and other low molecular weight hydrocarbons (Seitz et al., 1987; Wopenka and Pasteris, 1987; Lu et al., 2008). Methane plays a critical role in sediment geochemistry but is not directly detectable in situ by existing techniques. Paull and Ussler (2001) have shown by comparison of conventionally recovered cores and pore water sampling with pressurized core recovery that very large losses of methane (up to $\times 10^3$) can occur on recovery and thus an in situ technique is highly desirable. Similar problems likely occur, although to a lesser degree, with loss of sulfide during recovery since simple sense of smell usually indicates the loss of gas. Both methane and sulfide have strong Raman signals (Berger et al., 1995; Lu et al., 2008), with the symmetry of methane and the strong Raman cross section of the C–H bond making it a particularly useful target. Sulfide species co-exist in multiple forms in solution, and each of these has a characteristic Raman spectral signature.

2. Technical background

The Raman effect is the inelastic scattering of monochromatic light from a target molecule, providing information on both the composition and the structure of the molecular environment (Nakamoto, 1997; Ferraro et al., 2003). The rapid development of laser Raman spectrometers has resulted in their widespread use in the study of a variety of chemical systems (McCreery, 2000), and provides new opportunities for remote sensing of chemical processes in deep-sea research (Brewer et al., 2004; Pasteris et al., 2004). Scientists and engineers at the Monterey Bay Aquarium Research Institute (MBARI) have now developed a second generation of deep-ocean Raman in situ spectrometer (DORISS II) for in situ geochemical studies in the deep ocean (Fig. 1). DORISS II is based on a laboratory model laser Raman spectrometer (LRS) from Kaiser Optical Systems, Inc. (KOSI) (Owen et al., 1998). The core components of DORISS use a KOSI Raman RXN optical bench f/1.8i spectrometer by KOSI, a front-illuminated cooled 2048 × 512 CCD camera by Andor Technology, and a 532 nm frequency-doubled Nd:YAG laser. The spectrum is split into two stripes on the face of the camera by a duplex grating, enabling measurement of the full spectral range from 100 to 4000 Δcm^{-1} with $\sim 2\,\Delta\text{cm}^{-1}$ resolution. Neon and tungsten lamps were used for wavelength and intensity calibration on deck. The delivered laser power was ~60 mW and laser wavelength was calibrated against the 801 Δcm^{-1} Raman line of cyclohexane. All the spectra were acquired by KOSI's HoloGRAMS® software and saved in generic spectrum (.spc) format. The DORISS I and II systems have been deployed dozens of times on an expeditionary basis for in situ measurement of dissolved gases in the ocean, for the structure and composition of hydrates and for hydrothermal/cold seep minerals and fluids (Dunk et al., 2005; Hester et al., 2006; White et al., 2006b; Hester et al., 2007b).

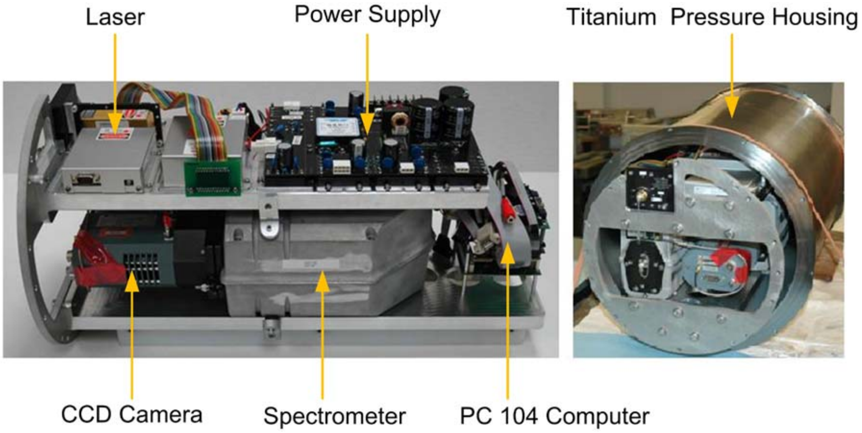

Fig. 1. The second generation of the deep-ocean Raman in situ spectrometer (DORISS II) showing the laser, spectrometer, CCD camera, on board computer, and power supply mounted on two-layer aluminum platform (left) inside the titanium pressure housing (right). The housing is 762 mm long, 305 mm diameter, and weight 140.6 kg (in air) and is mounted in the ROV tool sled.