Development of an In Situ Raman Spectrometer for Measurement of Sediment Pore Water Geochemistry in a High-pressure Reaction Cell

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***ABSTRACT* - We have developed and tested a novel in situ Raman spectrometer for geochemical studies of marine sediment pore water at a high-pressure reaction cell. With the high-pressure reaction cell, we can simulate appropriate pressure and temperature of the deep ocean up to 2000 m depth with 1-25 ^{o}C temperature range. A novel pore water Raman probe has been installed inside the high-pressure reaction cell, allows detailed measurement of the dissolved CH_4, SO_4^{2-}, H_2S, and pH inside the sediment pore water. Our particular interest for this device is to study the sediment pore water geochemistry change during the formation of the natural gas hydrate.**

I. INTRODUCTION

The Raman technique has been used in deep-ocean science since 2004. The engineering and science staff at Monterey Bay Aquarium Research Institute (MBARI) have developed, deployed, and tested a Deep Ocean Raman In Situ Spectrometer (DORISS) on the remotely operated vehicle (ROV) platform [1-3] and has been used to detect the hydrothermal vent and cold seep fluids[4].

Based on DORISS system, an in situ deep-sea Raman probe had been developed for marine sediment pore water geochemical studies [5]. This novel device allows detailed measurement of dissolved CH_4, SO_4^{2-}, H_2S and pH inside of pore water profiles in situ without incurring artifacts due to the degassing that typically occurs with core recovery pore water profiles [6-8].

Furthermore, DORISS system has also been used to detect the structure and composition of complex gas hydrates both occurring naturally on the sea floor and in controlled sea floor experiments designed to simulate the growth of such natural systems [9-12]. But, the sea floor controlled experiments for simulate the growth of natural gas hydrate will need a lot of ship time with the support of ROVs. It is really expensive. Furthermore, we cannot control the press-temperature condition in the deep-ocean to quick or slow the formation of the natural gas hydrate.

In this paper, a high-pressure reaction cell has been used to simulate the changeable press-temperature condition in the deep-ocean. Really deep sea marine sediment will be put inside this cell, the dissolved concentration of CH_4, SO_4^{2-}, H_2S, and pH of the sediment pore water can be monitored by a novel in situ Raman system in lab.

II. CONCEPTUAL DESIGN

As showing at Fig. 1, the conception of the in situ Raman spectrometer for sediment pore water geochemistry is based on a lab laser Raman system. The laser and Raman spectroscopy with CCD have been set up at normally lab environment. One single fiber has been used to connect the immersion optic and the laser for excitation, another as the connecter between the immersion optic and the Raman spectroscopy for collection. Both of the fibers are a part of a MR Probe filtered probe head, which can provide high signal-to-background measurements at any length of optical fiber.

An immersion optic has passed through the high-pressure reaction cell to collect the pore water spectra in situ. Inside the high-pressure reaction cell, a homemade sediment pore

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water drawing system has been designed. Four sintered stainless steel filters had been buried in the cell at different depth of sediment from 1m to surface, and connected with a valve. The valve will control which filter is connected to an optical micro-cell. When this system working, a small volume (around 1 milliliter) of pore water will be pulled though the filter by a manual pump and passed through a long micro-tube before transfer to the optical micro-cell for spectral analysis. Only 3 milliliter pore water is required for one Raman measurement. Once a measurement has been made, the volume will turn to connect with another filter and the existing fluid is withdrawn from the cell as the next sample is drawn in.

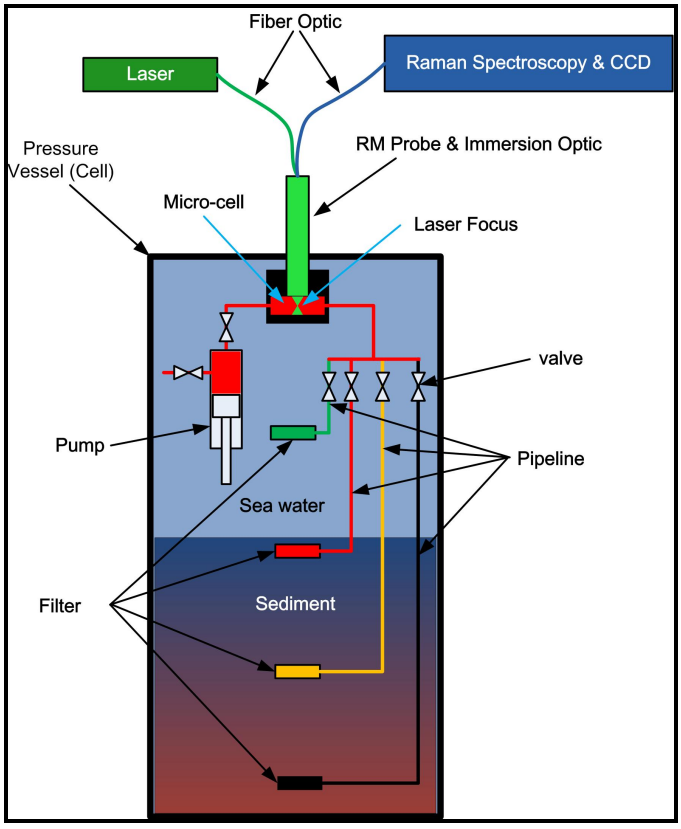

Figure 1. The concept design of the in situ Raman spectrometer for sediment pore water geochemistry

III. Lab System Development

Based on the initial concept of the in situ Raman spectrometer sediment pore water geochemistry has shown in front, engineers and scientists at Institute of Oceanology, Chinese Academy of Sciences (IOCAS) have successfully developed of this lab simulate device at 2013.

A customized laboratory model laser Raman spectrometer (LRS) from Kaiser Optical Systems, Inc. (KOSI) has been used for this device (Fig. 2). This LRS include a KOSI Raman RXN1 optical bench f/1.8i spectrometer, with a upgrade front-illuminated cooled 2048×512 CCD camera (the standard is 1024×128 CCD) by Andor Technology, and a KOSI 532 nm frequency-doubled Nd:YAG laser (Fig. 2a). The spectrum is split into two lines on the face of the camera by a duplex grating, enabling measurement of the full spectral range from 100 to 4325 Δ cm^{-1} with ~3.5 Δ cm^{-1} resolution. An immersion optic with a MR probe filtered probe head has been used for reaction monitoring (Fig. 2b); a long (3 mm from the window) data collection zone has be selected because it maximizes the signal intensity by using the entire effective focal cylinder (Fig. 2c); the tip of the immersion optic can work at -30 to +450°C temperate range with up to 3000 PSI pressure. All the spectra were acquired by KOSI's Holo-GRAMS software and saved in generic spectrum (.spc) format.

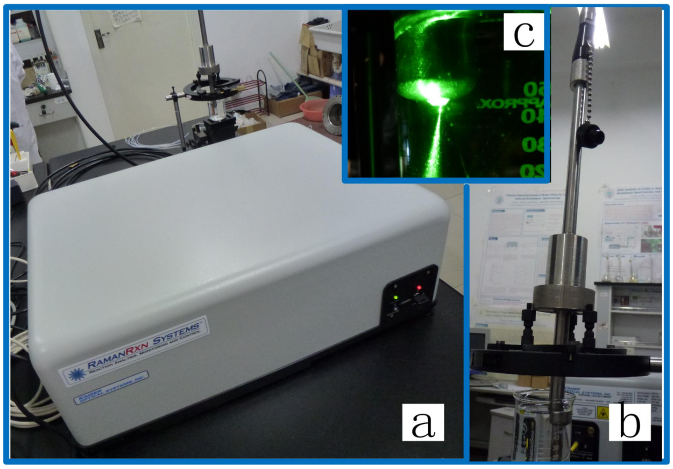

Figure 2. The customized laboratory model of laser Raman spectrometer. (a): the KOSI Raman RXN1 optical bench f/1.8i spectrometer, (b): the immersion optic with a MR probe filtered probe head, (c): the long (3 mm from the window) data collection zone of the immersion optic.

Because the inside diameter (ID) of high-pressure reaction cell only 180 mm, there are no standard devices can be choice for the sediment pore water drawing system. So, a homemade sediment pore water drawing system had been designed and

developed for fit the small ID of the reaction cell, showing at Fig. 3. A 4-way valve had connected with the sintered stainless steel filters by micro-tube inside the reaction cell (Fig. 3b). A handle had passed in the outside of the reaction cell through the wall of the reaction cell to control which filter will be opened to the pore water drawing system (Fig. 3a). The pore water will be draw out from the sediment with the force that generated by a manual reciprocating plunger pump (Fig. 3). Between the 4-way valve and the manual pump is an optical micro-cell with a KOSI immersion optic for the pore water Raman spectra collection in situ. Because the KOSI immersion optic cannot be machining, we have to design a very special stopper in the outside of the reaction cell to resist the inside 3000 PSI pressure.

All of the parts were made by stainless steel and go through the Quench-Polish-Quench (QPQ) process to prevent seawater corrosion.

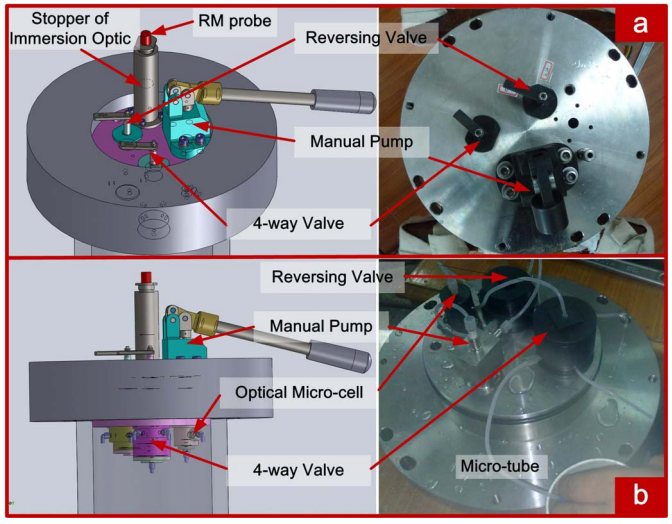

Figure 3.The homemade sediment pore water drawing system. (a): the outside structure of high-pressure reaction cell. (b): the inside structure of high-pressure reaction cell.

IV. System Initial Test Result

This homemade in situ Raman spectrometer system has been assembled and tested on the lab since July, 2013.

Firstly, we use the simulated sediment with standard seawater filled up the high-pressure reaction cell to test the whole system. Fig. 4 shows out the pore water Raman spectrum drawing from those simulated system. Three main Raman peaks has been showed out in this pore water Raman spectrum (Fig. 4). Two peaks are from water [13], the water H–O–H bending mode (ν_2, ~1640 Δcm^{-1}) and O-H stretching modes (~3615 Δcm^{-1}). The third peak is the S–O stretch (~981 Δcm^{-1}) of the sulfate ion.

In situ detection of the sulfate is of critical interest for the sulfate–methane interface (SMI). The SMI is a basic biogeochemical signal in methane-rich and methane-gas-hydrate-bearing marine sediments [14-16], so the sulfate in sediment pore waters contains important geochemical information.

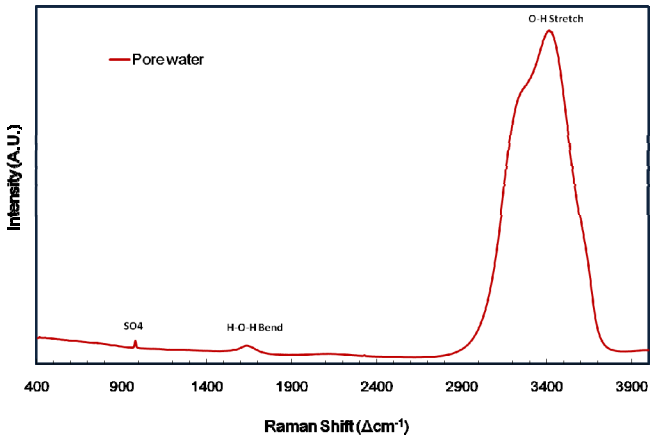

Figure 4. Raman spectra of pore water drawing from the standard seawater (P-series IAPSO, salinity = 34.992, sulfate = 28.9 mM) from 400-4000 Δcm^{-1} at 20 °C.

The high methane gas (983.4 PSI) also has been charged inside the reaction cell. Fig. 5 shows the Raman spectrum of pore water drawing from the saturated methane water solution (831.4 PSI at 16.8 °C) from 2500-4000 Δcm^{-1}. Only two significant Raman peaks has been shown out, one peaks is from water [13], O-H stretching modes (~3615 Δcm^{-1}). The second peak is the dissolved CH_4 with a Raman shift of 2910 Δcm^{-1}.

Unlike the normal sea water spectrum, there is some pore water fluorescence spectrums observed between 2900-4000 Δcm^{-1} for some reasons.

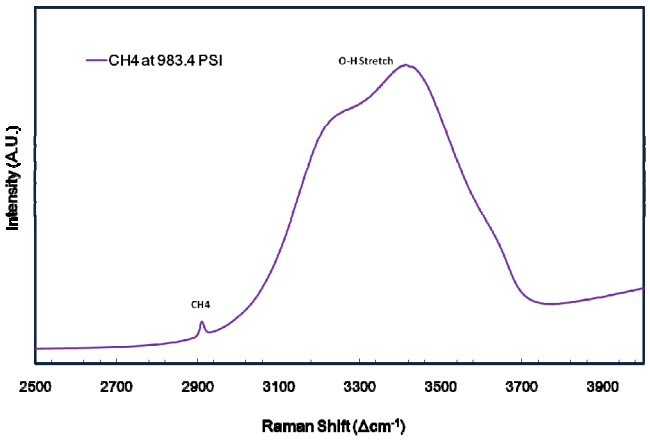

Figure 5. Raman spectra of pore water drawing from the saturated methane water solution (831.4 PSI at 16.8 ºC) from 2500-4000 Δcm^{-1}.

V. Conclusions And Future Work

The development of the in situ Raman spectrometer offers a new way to measure the sediment pore water geochemistry in high-pressure reaction cell. It is very useful tools for detailed measurement of the dissolved CH_4, SO_4^{2-}, H_2S, and pH inside the sediment pore water. This device will be used to study the sediment pore water geochemistry change during the formation of the natural gas hydrate in the future.

But, this lab simulates system just finished the development and initial test. A lot of works still need to be done for detail testing and standardizing this system in the lab. We only get some Raman peaks right now, and have no quantitative information such the concentration et al.; extended this system to the quantitative measurement of the dissolved CH_4, SO_4^{2-} and H_2S in the pore water will be our mission in the nearly future.

Acknowledgement

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