

Development of a new deep-sea hybrid Raman insertion probe and its application to the geochemistry of hydrothermal vent and cold seep fluids



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ABSTRACT

Hydrothermal vent fluids, cold seep fluids, their associated chemosynthetic communities, and the biogeochemical anaerobic oxidation of methane (AOM) play very important roles in the biogeochemical sulfur and carbon cycles in the ocean. Based on our previous success developing and deploying a deep-sea sediment pore water Raman probe, we developed a new deep-sea hybrid Raman insertion probe (RiP) designed to operate at temperatures up to 450 °C that can be inserted directly into high-temperature fluids emerging from hydrothermal vents. By routinely exchanging the various tips and optics of the probe, we can analyze the geochemistry of hydrothermal vent fluids, cold seep fluids, and sediment pore water profiles (0–60 cm) *in situ*. The instrument ensemble also includes a new deep-sea laser Raman spectrometer in a custom-designed, 6000-m titanium pressure housing, which is powered, controlled and deployed by the remotely operated vehicle (ROV) *Faxian* down to a maximum water depth of 4500 m. The new RiP was deployed at the Izena Hole hydrothermal area in the middle Okinawa Trough back-arc basin; the Papua–Australia–Canada–Manus (PACManus) hydrothermal vent area in the Manus back-arc basin, Papua New Guinea; and a cold seep field at Formosa Ridge in the northern South China Sea. The Raman peaks of CO₂, CH₄, H₂S, HS⁻, SO₄²⁻ and S₈ were obtained *in situ* from high-temperature hydrothermal vents (290 °C), low-temperature cold seep fluids (2 °C) and the surrounding sediment pore water. Dissolved CH₄ and S₈ were identified for the first time in the fluids under the lush chemosynthetic communities of the cold seep. Several sediment pore water profiles collected near the cold seep were characterized by the loss of SO₄²⁻ and increased CH₄, H₂S and HS⁻ peaks. Additionally, the *in situ* pH range of the pore water profile was between 6.95 and 7.22. Thus, the RiP system provides a very useful tool for investigating the geochemistry of hydrothermal vent and cold seep fluids.

1. Introduction

Following our successful development and deployment of a deep-sea sediment pore water Raman probe (Zhang et al., 2010), we showed that multi-element profiles of CH₄, SO₄²⁻, H₂S, HS⁻ and pH in sediment pore water can be collected rapidly and *in situ* at ocean depths (Peltzer et al., 2016; Zhang et al., 2011). Target species were quantified by normalizing observed signals to the ubiquitous water peak in the Raman spectra (Dunk et al., 2005). *In situ* measurements of pore water CH₄ concentrations in hydrate-rich ocean sediments revealed approximately 30-fold greater abundances relative to those in the recovered cores. Very large CH₄ losses occur during sample recovery (Zhang

et al., 2011). Peltzer et al. (2016) extended this technique to determine the total dissolved sulfide concentration *in situ*. Furthermore, the *in situ* pore water pH can be obtained by treating the HS⁻:H₂S doublet as a pH-indicating “dye”.

In addition to the pore water geochemistry, Raman spectroscopy has also been used for the *in situ* identification of rocks and minerals on the seafloor (White et al., 2006); the *in situ* detection of biologically precipitated solids such as bacterial mats and clamshells (White et al., 2006); the direct detection of CH₄ hydrates (Hester et al., 2007); the detection of dissolved CO₂ in seawater (Dunk et al., 2005); and the laboratory analysis of 1,4-thioxane, a chemical weapons breakdown product present in seawater (Zhang et al., 2009).

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The above discussion shows that since the first deep-ocean laser Raman *in situ* spectrometer (DORISS) was sent down to the seafloor at a depth of 3600 m in 2004 (Brewer et al., 2004), most of the targets mentioned by Brewer et al. (2004) as potentially suitable for Raman sensing have been explored using the DORISS I and II systems (Zhang et al., 2012). However, the use of Raman spectroscopy in hydrothermal vents and cold seep fluids has long been thought to be a challenge (Breier et al., 2010; Brewer et al., 2004; Zhang et al., 2012). White et al. (2006) used the DORISS I system for *in situ* analysis of hydrothermal vent fluids at the Sea Cliff Hydrothermal Field. However, only the SO_4^{2-} band was observed in the vent fluids. This limitation occurs because few optical systems are available that can endure the high temperatures of hydrothermal vent fluids (up to 400 °C). Additionally, the fluorescence backgrounds associated with organic materials in cold seep fluids and sulfide minerals in hydrothermal vent fluids overlap with the weak Raman signals. Moreover, CH_4 gas bubbling from cold seeps readily combines with seawater to form gas hydrates on optical surfaces. The minerals dissolved in high-temperature hydrothermal vent fluids precipitate as the temperature decreases, and they adsorb on optical surfaces; these phenomena reduce the optical transmission very quickly.

Furthermore, the geochemistry of cold seep fluids is strongly associated with the anaerobic oxidation of methane (AOM), which is the one of the most important biogeochemical processes linking the biogeochemical sulfur and carbon cycles in the ocean. The critical components of the diagenetic AOM reaction are well suited for Raman sensing (Zhang et al., 2011). However, to date, direct *in situ* Raman measurements of cold seep fluids have not been reported.

Few sensors can be directly inserted into high-temperature and high-pressure hydrothermal vents, which are also often strongly acidic. Most previously used sensors were based on electrochemistry and were typically able to detect only single chemical species (Ding and Seyfried Jr., 1996; Ding et al., 2005). Recently, with advances in detection methods and platforms such as ROVs and autonomous underwater vehicles (AUVs), several new techniques have been applied to investigate deep-sea geochemical processes. An *in situ* laser-induced breakdown spectrometer (Chemi-Cam) has been used for detecting seawater and mineral deposits in a hydrothermal vent field (Thornton et al., 2015). Additionally, an *in situ* mass spectrometer and several *in situ*

electrochemical sensors have been used to detect multiple parameters of diffuse hydrothermal fluids and their links to biogeochemical processes (Gartman et al., 2011; George et al., 2012; Luther et al., 2001; Wankel et al., 2011; Zielinski et al., 2011). The *in situ* detection of CO_2 and CH_4 seeps on the seafloor using infrared spectroscopy has been investigated (Schmidt et al., 2013, 2015). However, none of these probes can be directly inserted into the high-temperature fluids emerging from hydrothermal vents.

In this paper, we describe the development of a series of Raman insertion probe (RiP) systems and their deployment in the Izena Hole hydrothermal area in the middle Okinawa Trough back-arc basin; the PACManus hydrothermal area in the Manus back-arc basin, Papua New Guinea; and a cold seep field in the northern South China Sea (Liu et al., 2008; Reeves et al., 2011; Thal et al., 2014).

2. Methods

2.1. New hybrid Raman probe development

The previously developed deep-sea pore water Raman probe (Zhang et al., 2010) was successfully applied to the measurement of sediment pore water multi-element profiles (Peltzer et al., 2016; Zhang et al., 2011), but it could only be used to analyze low-temperature fluids. The challenge addressed in this work was to design a probe that could be directly inserted into the high-temperature fluids emerging from a hydrothermal vent (up to 450 °C) and that could be used to determine the geochemistry of cold seep fluids and sediment pore water profiles by routinely exchanging various tips and optics.

2.1.1. Concept design

A conceptual design of the new hybrid Raman probe for achieving these goals is shown in Fig. 1. Two sets of tips and optics are used for high-temperature and low-temperature deployments, and they can be easily exchanged at sea.

The upper left panel in Fig. 1 shows the system used for high-temperature hydrothermal vent fluids: the RiP-Hv probe. The sulfide minerals found in most vent fluids can easily separate out and adsorb onto exposed optical surfaces, thereby decreasing the Raman signal. Therefore, a sintered stainless steel filter with a pore size of 2 μm was

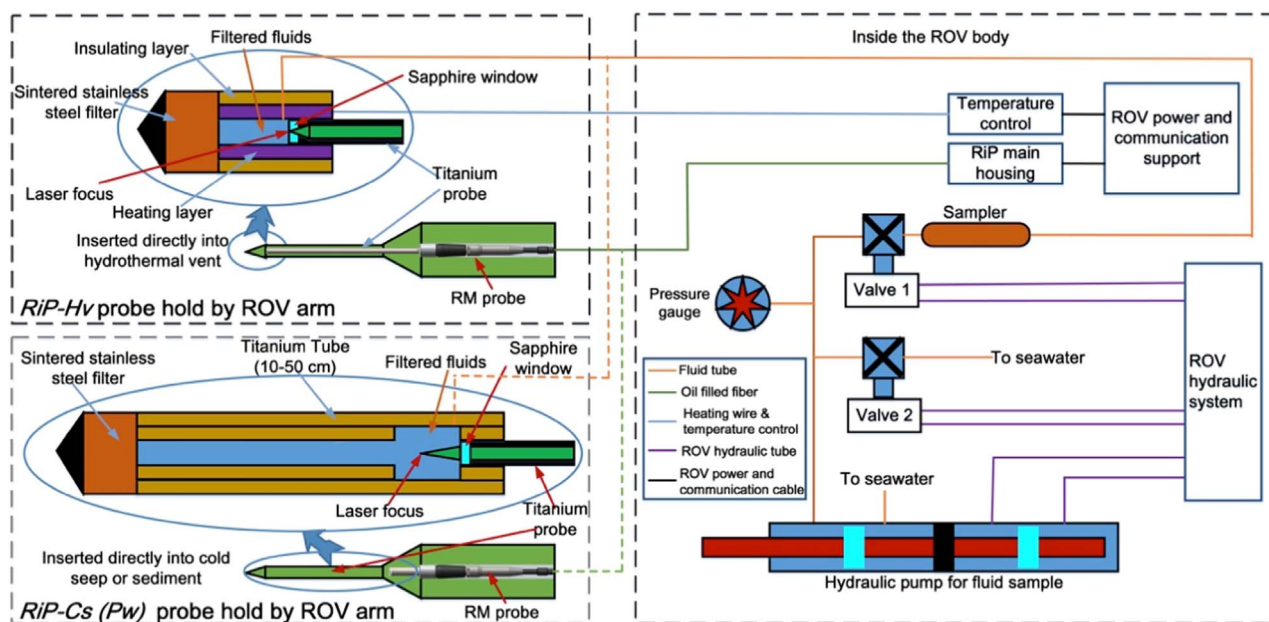


Fig. 1. The design of the RiP system. The RiP-Hv probe used to investigate hydrothermal vent geochemistry is shown in the upper left panel, with solid lines indicating the connections to the ROV body. The RiP-Cs (Pw) probes for studying cold seep fluids and sediment pore water geochemistry are shown in the lower left panel, with dashed lines indicating the connections to the ROV body. The RiP-Hv and RiP-Cs (Pw) probes can be easily exchanged at sea.

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