In Situ Raman Spectra from the SeaCliff Hydrothermal Field (Gorda Ridge)

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OS43B
0558

Abstract

MBARI's *in situ* laser Raman spectrometer (DORISS – Deep Ocean Raman *In Situ* Spectrometer) was deployed at the Sea Cliff Hydrothermal Field on the Gorda Ridge in July 2004. The first *in situ* Raman spectra of hydrothermal minerals and high-temperature fluid venting from the seafloor were obtained. These spectra are analyzed and compared to laboratory measurements of samples collected from the site.

Laser Raman spectroscopy is a proven, powerful geochemical technique for analyzing the chemical composition and molecular structure of solids, liquids, and gases. During an expedition to Gorda Ridge on the *R/V Western Flyer* in July 2004, DORISS was deployed successfully by the *ROV Tiburon* at hydrothermal vents on the seafloor (~2700 m depth). Data were collected from hydrothermal fluids, chimney minerals (e.g., anhydrite and barite), and bacterial mats using two types of sampling optics – an immersion optic, and a non-contact optic. To collect spectra from opaque mineral samples, a precision underwater positioner (PUP) was used to position the DORISS probe head. PUP is a stand-alone, three degree-of-freedom positioner capable of moving the DORISS probe head with a precision of 0.1 mm (required by the small focal volume of the sampling optic).

Raman spectra were collected of ~300° C vent fluids with both sampling optics. The Raman spectrum of seawater contains bands from the bending (~1640 cm^{-1}) and stretching (3000-3700 cm^{-1}) vibrational modes of the water molecule and a small peak from the S-O stretch of the sulfate ion (~981 cm^{-1}). Compared to ~2° C ambient seawater, vent fluid spectra show changes in the intensity ratios of the water bands due to the elevated temperature, and the sulfate peak is reduced. Additional components of hydrothermal fluid are present in such low concentrations that it is difficult to detect them with the current Raman system. The chimneys in the Sea Cliff field are primarily anhydrite, and debris in the area also contains barite. We were able to obtain quality spectra of both anhydrite (primary peak at ~1017 cm^{-1}) and barite (primary peak at ~987 cm^{-1}). In addition, we were able to detect elemental sulfur in the polycrystalline S_8 morphology which may have been produced by bacterial mats (peaks at ~218 and 473 cm^{-1}).

Geologic Setting

The Sea Cliff Hydrothermal Field is located on the northern end of the Gorda Ridge, an intermediate rate (~55 mm/yr) spreading segment in the northeastern Pacific Ocean (below). Hydrothermal activity is located approximately 2.6 km east of the spreading axis at a depth of 2675-2800 m (~300 m above the axial valley floor). The site was first identified by water column anolamies in 1986, and first visited by the U.S. Navy submersible *Sea Cliff* in 1988.

Active venting is concentrated along ridges which trend perpendicular to the slope of the eastern axial valley wall (022°). The chimneys formed along these ridges are primarily composed of anhydrite and smectite with minor sulfide phases. The seafloor in the area is covered with a hydrothermal crust which consists of altered basalt, barite, amorphous silica, and sufides. Large areas of the vent field between the chimney ridges are covered with blue mat-like material believed to be a type of ciliate. The vent fluids were essentially clear with temperatures up to ~300°C. The fluids have been found to be low in salinity and sulfide content. (Data from recent observations was presented on poster T21C-0538).

Gorda References

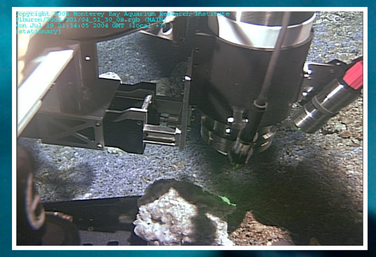
Rona & Clague, Geologic controls of hydrothermal discharge on the northern Gorda Ridge, *Geology*, 17: 1097-1011, 1989.

Rona, et al., Major off-axis hydrothermal activity on the northern Gorda Ridge, *Geology*, 18:493-406, 1990.

Zierenberg, et al., Alteration of basalt hyaloclastite at the off-axis Sea Cliff hydrothermal field, Gorda Ridge, *Chemical Geology*, 126:77-99, 1995.

Background Picture: The DORISS probe head being positioned at a hydrothermal vent by the ROV Tiburon manipulator at the Sea Cliff Hydrothermal Field, Gorda Ridge.

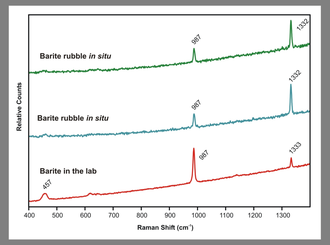
Operations

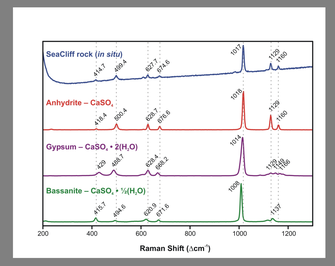


The Precision Underwater Positioner (PUP - picture at left) was used to position the probe head at the target of interest (picture above). PUP consists of a tripod frame and three actuators providing 3 degrees of movement – Z axis (up-and-down), R-axis (in-and-out), and theta axis (rotation about the Z axis. A camera, light, and red lasers that cross at the DORISS focal point assist the scientist in positioning the probe head. PUP and DORISS are controlled by ship-board scientists.

Hydrothermal Minerals

PUP was used to position the DORISS probe head at rock samples on the seafloor. In some cases, chimney material was broken off onto the ROV porch and analyzed there. Two minerals were primarily observed with the DORISS instrument. When analyzing hydrothermal crusts and rubble in the vent field we detected barite ($BaSO_4$). This mineral was mostly found as thin rinds or veins around darker material which exhibited significant fluorescence.





The chimney structures were primarily anhydrite ($CaSO_4$). Because anhydrite is soluble in cold seawater, it was not observed away from the high-temperature chimneys. There are two forms of hydrated calcium sulfate: gypsum ($CaSO_4 \cdot 2(H_2O)$) and bassanite ($CaSO_4 \cdot \frac{1}{2}(H_2O)$). These three calcium sulfate species can be distinguished from their Raman spectra. The figure on the right compare spectrum from a Sea Cliff sample to the spectra of anhydrite, gypsum and bassanite. The sample is clearly anyhydrite.

References

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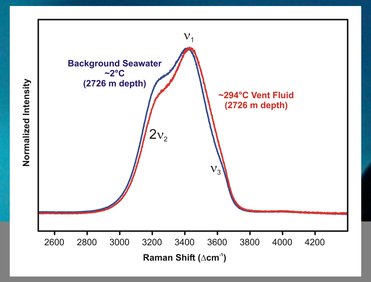
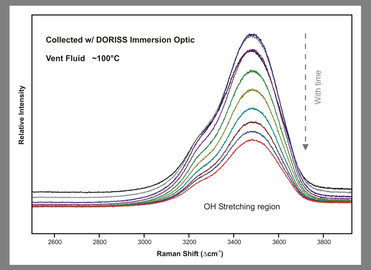
Hydrothermal Vent Fluids



Comparison of ambient seawater and hydrothermal fluid spectra in the O-H stretching.



Vent fluid spectra (in the O-H stretching region) over time.

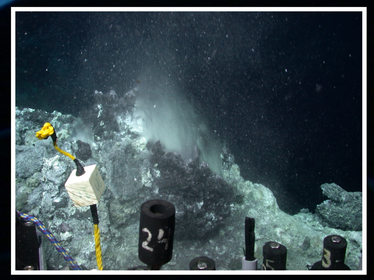
Using *in situ* Raman spectroscopy, we hoped to be able to detect various constituents of hydrothermal vent fluid such as gases like CO_2 and H_2S. The Raman spectrum of seawater is composed of bands due to the bending and stretching of the water molecule, and a peak at ~981 cm^{-1} due to the sulfate ion. The stretching bands of the water molecule are affected by both temperature and pressure.

We obtained a number of spectra of vent fluid using two configurations (discussed at right). In all cases we observed changes in the region of the O-H stretching modes of water due to the elevated temperature of the hydrothermal fluid (top right). In ambient seawater at 2627 m depth, the ratio of the areas of the 2 , band to the , band is ~0.75. For hydrothermal fluid the ratio was ~0.65.

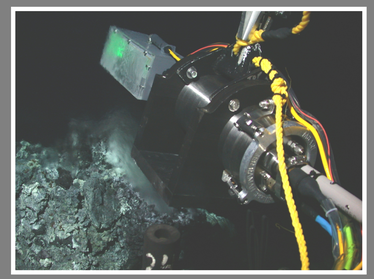
When using the immersion optic configuration (lower right picture) we found that the intensity of the Raman spectra decreased over time (lower left). This was due to the fact that the sapphire pressure window of the optic was immersed in the vent fluid and a light sulfide coating built up on the window. Although the fluid was ~294°C as it exited the chimney orifice, it was reduced to ~100°C (as measured by a thermocouple in the top of the box) by the time it was in the box due to entrainment of ambient seawater.

The other major observation was the decrease in or lack of a signal from the sulfate ion. This is because vent fluid is stripped of sulfate in the subseafloor.

We did not see peaks characteristic of CO_2 or H_2S. Vent fluid samples collected during the dive were analyzed by Karen Von Damm at UNH and showed...

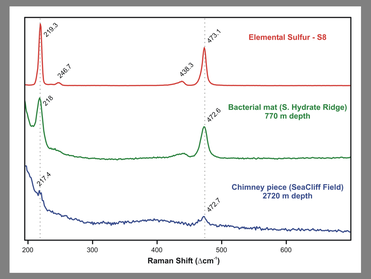


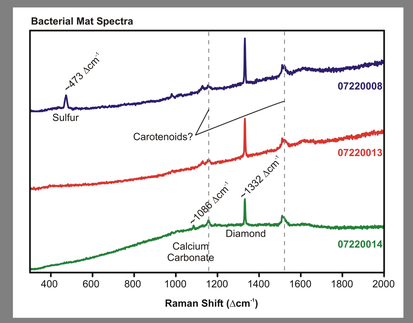
Vent fluid (above) was analyzed on two dives. On the first dive, a stand-off optic was used behind a dome window which was not in contact with the hydrothermal fluid; thus some seawater was in the optical path. The focal point was positioned inside the volume of exiting fluid using the ROV manipulator. On the second dive, the immersion optic was used protruding into an open-bottomed box. The box was held over the vent to collect the buoyant hydrothermal fluid. In this case the optic window was immersed in the vent fluid.



Biological Material

Bacterial mat spectra was obtained at both the Sea Cliff Hydrothermal Field, and Hydrate Ridge. Previous laboratory studies of bacterial mat using Raman spectroscopy showed that the bacteria produced elemental sulfur in an S_8 morphology. *In situ* spectra collected from Gorda Ridge and Hydrate Ridge both correspond well to S_8 elemental sulfur (below). The spectrum from Hydrate Ridge (green) was collected using PUP to focus DORISS on seafloor bacterial mat. The spectrum from Gorda Ridge (blue) was seredipitiously collected while trying to collect spectra from a chimney.





While collecting spectra from bacterial mats at South Hydrate Ridge, we detected other interesting materials. The three spectra above are from a scan across a bacterial mat on the seafloor. The top spectrum shows the characteristic sulfur band previously discussed. The bottom spectrum has a 1086 cm^{-1} band which is characteristic of calcium carbonate. Unfortunately, the weaker bands were not detectable. These band allow one to discriminate between calcite and aragonite (both $CaCO_3$). Additionally, all three spectra show bands at ~1154 and ~1520 cm^{-1}. These are characteristic of carotenoids which are known to be present in clam shells. Clams shells were in the area in which we were analyzing bacterial mats.

We attempted to collect Raman spectra from other biological targets as well. The blue mat-like material seen in the picture in the Operations section had no discernable Raman peaks but did exhibit strong fluorescence.

We also attempted to collect a Raman spectrum from a **tube worm** (*Ridgeia piscesae*) tube (above). We believe the tube to be chitinous. However no chitin Raman peaks were observed. We did observe two strong fluorescent bands. These bands were wide (~400-500 cm^{-1}), and the peak maximums were at wavelengths of 617 and 682 nm (excitation wavelength was 532 nm).