Laser Raman Spectroscopy as a tool for *in situ* bio-geo-chemical analyses in the deep ocean

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Oceanography has historically been a science based on the collection of samples for ship- or shore-based analyses. While disciplines such as phycial oceanography and seafloor seismology have transitioned to sensing rather than sampling, disciplines such as geology, chemistry and biology have lagged behind. The development of deep-sea platforms such as remotely operated vechicles (ROVs), autonomous under-water vehicles (AUVs), and cabled observatories is driving the need for instruments capable of *in situ*, autonomous, real-time measurements in the deep ocean. This is particularly true for extreme environments such as seafloor hydrothermal vent systems.

Laser Raman Spectroscopy is an optical technique capable of *in situ* molecular identification of solids, liquids and gases. A laser excites a target, and the spectrum of the energy-shifted, backscattered light provides compositional and strucutral information about the target. Raman scattering is a weak effect – only 1 in 10^8 photons is Raman scattered – but it benefits in the deep ocean from the lack of ambient light. Because it is non-invasive and does not require reagents or consumables, laser Raman spectroscopy is well-suited to remote, deep-sea environments.

While the potential is great, there are still a number of challenges to be addressed to effectively use laser Raman spectroscopy in the deep ocean. These include techniques to mitigate interference from fluorescence which can overwhelm the Raman signal; mechanisms to precisely position the laser spot; and approaches to extract background seawater signals from the spectra.

A sea-going laser Raman spectrometer, Deep Ocean Raman *In Situ* Spectrometer (DORISS), has been deployed to collect spectra of seafloor shells; bacterial mats and clathrate hydrates at cold seep sites; minerals at hydrothermal vent and seafloor slump sites; and dissolved gases in controlled dissolution experiements. Laboratory Raman analyses of mineral species (e.g. carbonates, sulfates and sulfides) and dissolved gases (e.g. CO_2 and CH_4) of interest in seafloor hydrothermal systems has been undertaken to determine how to optimize sea-going Raman systems for hydrothermal applications. The goal is the development of miniature Raman instruments capable of monitoring hydrothermal vent fluid chemistry and geochemical processes in vent plumes.

Mass-independent fractionation of sulfur isotopes during experimental photolysis of sulfur dioxide and carbonyl sulfide

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Sulfur mass independent isotope fractionation (MIF) has been observed in many Archean rocks. Photochemical reactions of atmospheric sulfur gases, particularly the UV photolysis of SO_2, remain the most likely source of these sulfur MIF signatures. Understanding the isotope effects of the various photochemical reactions of sulfur gases, both theoretically and experimentally, can help reconstruct the atmospheric chemistry of the early Earth.

Broad band photolysis of SO_2 using a Xe lamp has yielded $\delta^{33}S/ \delta^{34}S$ values of approximately 0.64. Additional photolysis experiments are being carried out on SO_2 using a 200±30 nm bandpass filter. This isolates the 180-230 nm absorption band of SO_2, which corresponds to the photodissociation of SO_2 into SO + O. Preliminary results show $\delta^{33}S/ \delta^{34}S$ values of approximately 0.62, similar to the fractionation caused by the full-spectrum photolysis. This suggests that 180-230 nm photodissociation is the primary cause of mass independent fractionation in SO_2 photolysis. Photolysis experiments on SO_2 using a 250 nm longpass filter are also being carried out to target the weaker photoexcitation band (260 – 340 nm) and exclude the strong SO_2 photodissociation band.

UV Photolysis of carbonyl sulfide (OCS) has shown small but measurable MIF signatures ($\delta^{33}S/ \delta^{34}S = 0.533$) [2]. Additional OCS photolysis experiments are being performed on OCS purified by gas chromatography and tested with full spectrum and 180-230 nm UV.

[1] Ono *et al.* (2009) *Eos Trans. AGU* **90**(52) Fall Meet. Suppl. Abstract V13G-05. [2] Lin *et al.* (submitted) *Geophys. Res. Lett.*