Tunable laser spectrometry ability on steroids to track ocean methane

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The problem of oceanic methane

Marine sediments are probably the largest repository of methane on earth but both data on ocean floor fluxes and details of processes of water column attenuation or additions are insufficient. Stable isotope compositions of methane C and H can identify formation processes while trends of changes show attenuation [1]. To progress we need to check sources and sinks to background levels in very many parts of the oceans. There have been attempts to develop a suitable instrument: Wankel et al. made major progress using IR absorption for carbon isotopes with integrated cavity output spectroscopy [2]. Dissolved methane is extracted by diffusion through a membrane. This analytical method has the demerit of fractionating the gas's molecular and isotopic composition. Also, the introduction of each sample is time consuming.

A potential solution to the problem

An emerging, new analytical technology, Capillary Absorption Spectrometry (CAS) [3] is a form of the Tunable Laser Spectrometer, as in the Curiosity rover on Mars [4]; however, instead of a Herriott cell of 100s of ml volume, the "cell" is the inside of a hollow 2 to 3 m long optical fiber (0.2 ml), enabling a 10,000× smaller sample but with similar sensitivity. This allows a different sampling system. The device we are developing takes a <1 ml whole water sample which is degassed for analysis within the pressure housing. The fiber is coiled to make it more compact.

Current tests and other CAS developments indicate that we should be able to analyze background methane and analyze fast enough to deploy the instrument on an AUV to locate and analyze seeps and vents. We have already demonstrated fast analysis but not yet finished tests for ultimate senitivity as the development is ongoing, but we will present our latest results at the meeting.

[1] Whiticar (1999). *Chem. Geol.* **161**, 291-314. [2] Wankel *et al.* (2013). *Env. Sci. Tech.* **47**, 1478-1486. [3] Kelly *et al.* (2013) *Proc. SPIE 8993, Nanophotonic Devices* **XI**, 899310. [4] Webster *et al.* (2018) *Science* **60**, 1093-1096.