1. Overview

Final Report

2023-12-29

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Membrane-free In-situ Underwater Gas Analyzer Using Laser Spectroscopy in a Compact Hollow Fiber Cell

Primary Area of Operation: Torrance, California

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Award period: From 09/01/2018 To 08/31/2023

Period Covered by this Report: From 09/01/2018 To 08/31/2023

2. Summary

2.1 Abstract

To meet the need for better analysis of ocean methane, we developed an in-situ gas sensor, that combines a novel laser absorption spectrometer with a membrane-free approach to water sampling. The sensor was designed for real-time measurements of methane concentration and isotope ratio at depths to 3000 m and is useful for scientific studies and energy exploration. A prototype of the sensor was produced and utilized on an ROV for in-situ measurements of methane at deep-sea vents, Figure 1. The system performed very well for methane concentration measurements, and future efforts are proposed for improving the time response and isotope ratio measurements.

Figure 1. In this project we produced an in-situ methane analyzer, which was deployed on the Jason ROV and used to measure methane from deep sea hydrothermal vents.

2.2 Purpose of Project:

2.2.1 Describe issue that was addressed:

Methane in the oceans has important implications for the global carbon cycle but determining relative contributions of specific sources is complex, Figure 2. This is hampered by the current slow, time-consuming approach of extracting discrete water samples that are later analyzed in a lab. Lab analysis is generally expensive and labor intensive and results in limited sample density over time and space. We addressed this need by developing a new tool that can quantify ocean methane in-situ, helping to attribute sources and improve understanding of relevant processes.

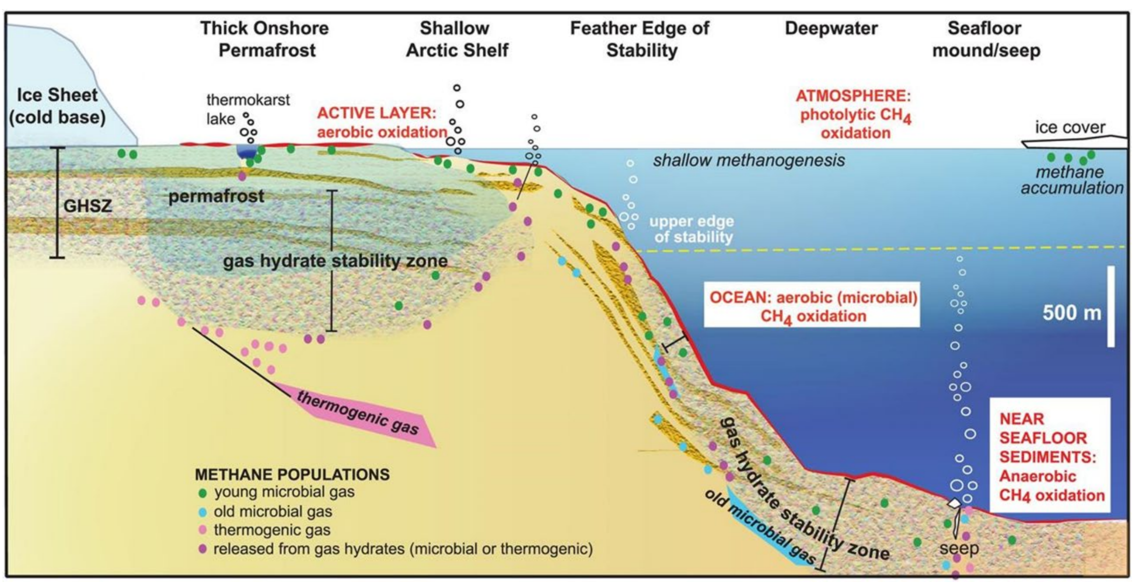

Figure 2. Methane sources are varied and not sufficiently characterized or inventoried (image source: https://handwiki.org/wiki/index.php?curid=1290021).

2.2.2 Describe/list the project objectives:

The primary objective of the project was to develop and demonstrate a new type of in-situ methane analyzer capable of measuring at depth. The sensor has two major components: (1) Hollow fiber-based laser absorption gas analyzer and (2) Membrane-free water sampler. The hollow fiber gas cell is proprietary to OKSI and is a unique technology upon which a range of trace-gas and isotope sensors are being pursued; it has an ultra-low sample volume (~ 1 mL), which is the feature that enables use of the membrane-free water sampler.

The specific technical objectives for the project included the following:

- Improve the water sampling front-end to enable sampling at depth and remote actuation
- Design a complete system for in-situ analysis using ROV power
- Package the system in an underwater, pressure housing capable of depth = 3000 m
- Develop software for control and data acquisition from ship deck
- Demonstrate initial breadboard in the lab with water samples (TRL 5)
- Field demonstration of prototype on a CTD Rosette (TRL 6)
- Complete demonstration of prototype at depth from an ROV (TRL 7).

All of these objectives were accomplished during the project, and the effort was highly successful in producing and demonstrating a new sensor concept. The in-situ methane concentration measurements worked very well. To build on this work, we are proposing follow-on efforts for AUV operation and improved isotope ratio measurements, see Section 3.3.

2.3 Approach:

2.3.1 Describe the work that was performed:

The sensor concept is based on tunable laser absorption spectroscopy (TLAS) in the mid-infrared (Mid-IR) wavelength range (λ ~ 2 to 16 μm), which is a highly selective and sensitive technique that is able to differentiate AND quantify a range of molecular species, including greenhouse gasses, volatile organic compounds (VOCs), Toxic Industrial Chemicals (TICs), and combustion products. In many applications a gas cell is used to provide a defined volume and/or to enable measurements at reduced pressure. Companies such as Picarro and Los Gatos Research (LGR) typically target weak absorption features in the near-infrared (NIR) wavelength range and use cavities to increase the effective interaction with a sample volume ~ 100 ml.

We developed a system that utilize a hollow fiber optic waveguide as its central gas cell, in a concept we refer to as a capillary absorption spectrometer (CAS)[1]. The hollow fiber is glass or plastic capillary with an internal diameter ranging from ID = 0.2 to 1.5 mm that is coated on the inside with a reflective coating optimized for Mid-IR wavelengths[2]. The fiber contains the gas under analysis and guides the probe laser beam from source to detector with near unity overlap between the beam and the analyte. The small volume, high interaction between analyte and incident light (i.e., high analytical sensitivity), and overall physical flexibility of the waveguide confer reduced footprint, power, and sample size requirements over related techniques and are directly applicable to field deployments and portable operations.

[1] J.F. Kelly, R.L. Sams, T.A. Blake, and J.M. Kriesel, "Further developments of capillary absorption spectrometers using small hollow-waveguide fibers", SPIE Proceedings Vol. 8993, DOI: 10.1117/12.2042734 (2013).

[2] C. M. Bledt, J. A. Harrington, and J. M. Kriesel, "Loss and modal properties of Ag/AgI hollow glass waveguides," Appl. Opt. 51, 3114-3119 (2012).

In general CAS sensor hardware consists of a tunable laser, a hollow fiber gas cell, a detector, electronics, and gas plumbing components. For in-situ, underwater methane analysis at depth, we also developed a novel sampling system and packaged the system in a pressure housing. The sampling approach enables measurement of dissolved gases without using a membrane, which are exceedingly difficult to calibrate. Instead, of a membrane the system conducts measurements by taking a discrete amount of water (~ 1 ml) into the pressure housing. This small "slug" of water is introduced into an evacuated chamber, which effectively "degasses" the methane and other volatiles (including water vapor). The small amount of evolved gas is sufficient to fill the hollow fiber gas cell of the CAS sensor, where a laser absorption signal is measured, see Figure 3. The whole system runs off of 24VDC and streams data in real-time via an ethernet connection to a remote operator.

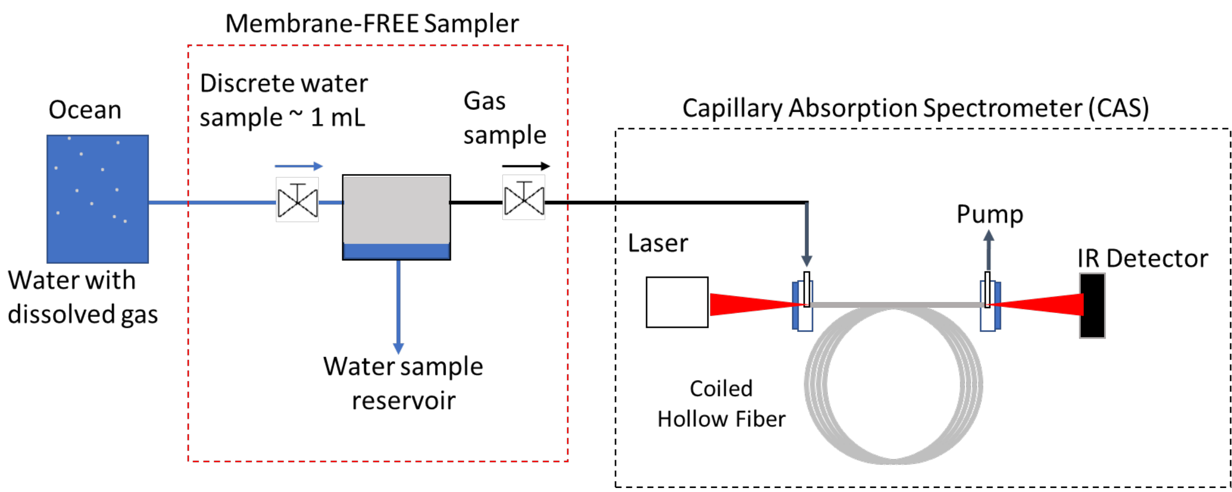

Figure 3. Diagram illustrating basic sensor concept. A membrane-free front end includes a pre-evacuated chamber in which gas is evolved from a water sample. The gas then travels to the CAS system and is analyzed utilizing tunable laser absorption spectroscopy.

- Cylindrical pressure housing
- Internal: 10" x 30"
- Tube OD = 11.3"
- Flange OD = 12.3"
- Depth Rating = 3000 m
- 7075-T6 Aluminum
- Weight in Air = 135 lbs
- Power = 75 Watts
- Voltage = 24 Volts

Figure 4. Picture of underwater housing designed and built for the CAS, alongside a list of specifications.

The effort built directly on proof of concept and lab prototypes developed under a NOAA SBIR project[3]. With this starting point, the project focused on engineering a system for in-situ analysis at depth, which included sourcing new parts, designing and procuring a pressure housing, assembling the system, testing, and iterating as needed. A picture of the system, along with specifications is shown in Figure 4.

Throughout the project, the system went through extensive testing in the lab, along with associated modifications to improve the functionality and performance. This included modifications to components (e.g., electrical power supplies), measurement approach (e.g., gas purging between water injections), and software (e.g., automated control of valves). OKSI verified high quality performance of the sensor with tests of methane concentration using a mixing manifold. The sensor performance was verified to be linear over concentrations from 5 to 200 ppm with an R2 = 0.99996 for $^{12}CH_4$ and R2 = 0.9993 for $^{13}CH_4$ measurements. Additional calibration measurements were conducted in conjunction with a Gas Chromatograph (GC) system, which provided further validation of the measurements, see Figure 5.

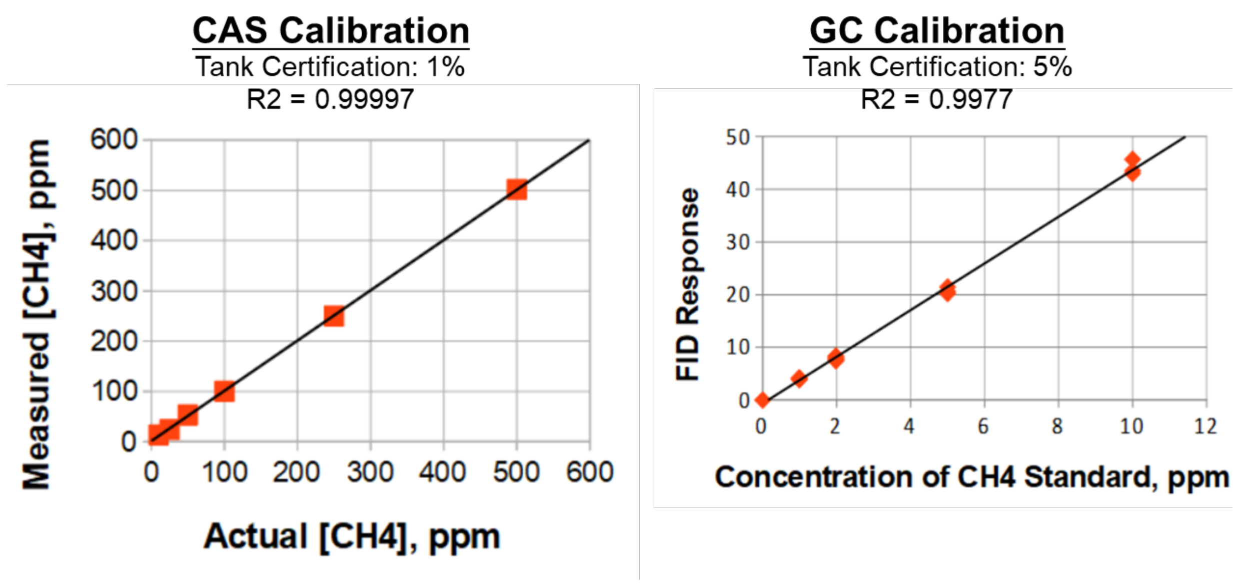

Figure 5. Calibration results of CAS as compared to Gas Chromatograph (GC) to which CAS results were compared.

OptoKnowledge conducted additional tests of system performance for the measurement of isotope ratios. With gas samples the isotope ratio precision was adequate (~ 1 per mil) with two different isotopic standards easily distinguished. There is drift in the measurement over time, but sufficient accuracy can be achieved by using calibration gas. With water samples the reproducibility error was determined to be too large, which we believe is due to fractionation issues associated with extraction of methane from the water samples. For this reason, additional work was conducted to improve the extraction; however, we feel that more work is still needed beyond this project to further improve the performance.

The underwater methane CAS was first demonstrated on a CTD Rosette analyzing methane concentration in the water column. The system ran off battery power and communicated with an

[3] SBIR Contract NOAA #WC133R17CN0059

operator aboard the host ship (Rachael Carson) via a custom 2-wire connection. The system was deployed over a two-day period in June 2021 with CTD casts to various depths at multiple locations in Puget Sound, Washington, see Figure 6. The tests provided a basic proof of concept of the performance with results agreeing very well with returned samples, see Section 2.4.1.

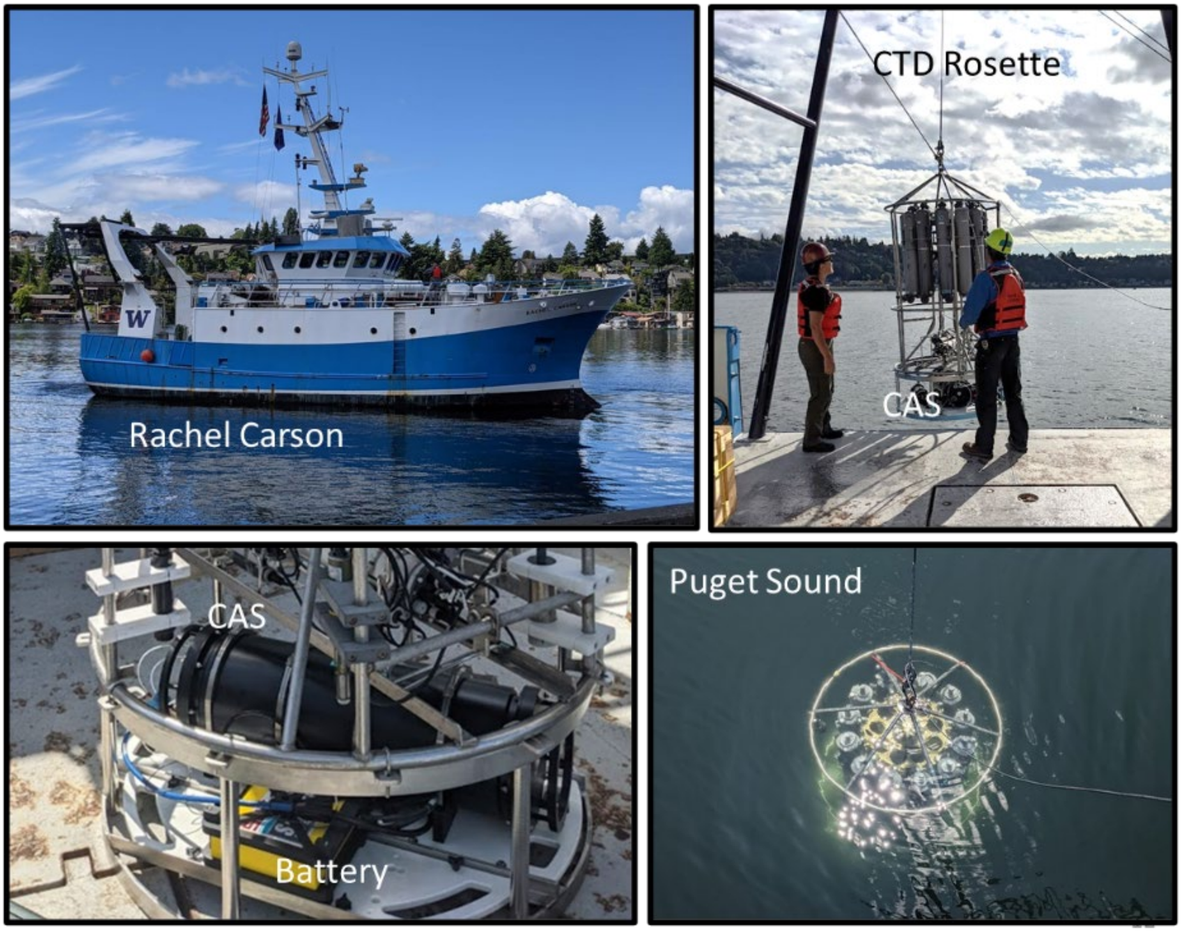

Figure 6. The underwater methane CAS was utilized to measure methane in Puget Sound, Washington in June 2021. The system was mounted on a CTD rosette with battery power.

Following installation on a CTD, the system was utilized on a remotely operated vehicle (ROV). Specifically, the CAS was installed on the Jason ROV utilizing on-board 24VDC power and an ethernet connection, see Figure 7. The system communicated directly with an operator aboard the host ship (R/V Thompson), which enabled control and real-time data visualization. The system was deployed on a cruise to Axial Seamount in the Pacific Ocean July 2022; however, the cruise was cut short due to an outbreak of COVID and only one dive was conducted.

Despite the shortened cruise, we were still successful at obtaining data with the ROV-CAS. In-situ methane measurements at vent sites are compared to off-line measurements of returned samples conducted with a GC. in Section 2.4.1. The system was demonstrated to accurately measure methane concentration with relatively high precision. Isotope measurements were also made with the in-situ system, but the results were not of high enough quality to be scientifically useful.

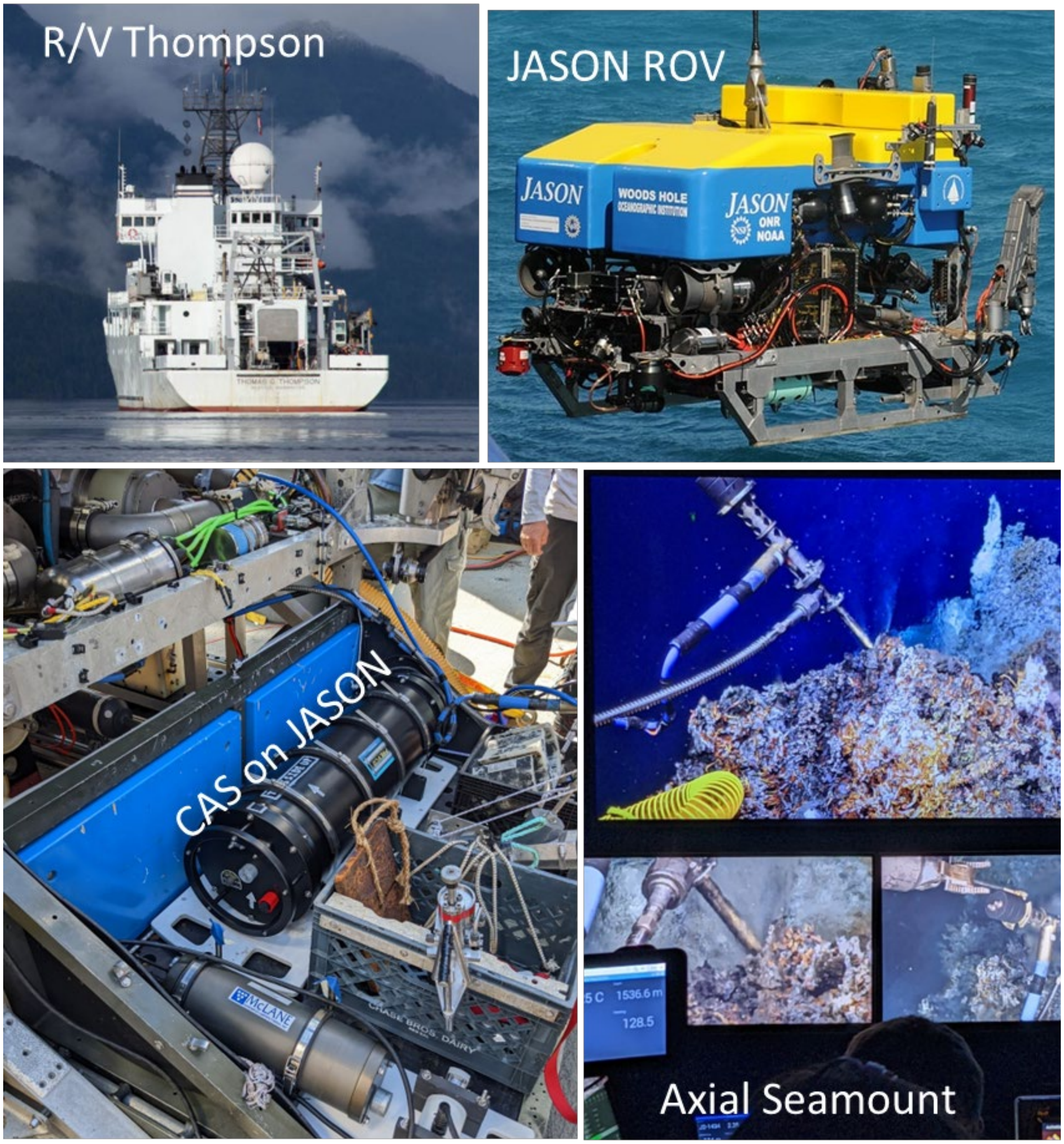

Figure 7. The CAS was mounted on the Jason ROV and utilized to measure vents at Axial Seamount in the Pacific Ocean off the coast of Oregon / Washington in July 2022.

2.3.2 Describe how the project was organized and managed:

OKSI was the primary sensor developer and oversaw the entire project. In addition, OKSI was specifically responsible for the CAS sensor development, system integration, and sensor operation including data acquisition, analysis, and user interface. JPL was originally responsible for developing the water sampling method and hardware; however, due to COVID-related delays; OKSI took over that aspect of the project as well. UW/OSU scientists guided the development from a scientific user perspective and also contributed to the design of the water sampling system. In addition, UW/OSU organized and managed field deployments including system integration on the CTD and ROV, as well as helping to collect, analyze, and interpret the CAS measurements and associated measurements with other instruments, e.g., Gas Chromatograph.

2.3.3 Describe how data was organized, processed, and archived:

Raw CAS sensor data was saved in OKSI's proprietary format and archived on their internal storage folders. The spectral data is processed into methane concentration and isotope ratio using LabVIEW code specifically written for this purpose. Additional data taken by OSU and UW with GC instruments and at the isotope lab in Zurich, were organized, processed, and archived following their standard procedures.

2.4 Findings:

2.4.1 Describe actual accomplishments and findings:

Prior to the CTD deployment of the sensor in June 2021, a one-day "reconnaissance" type cruise was conducted on March 31, 2021 to find sites with high methane concentration as targets for the CAS in-water test that followed in June. We found the highest concentrations at the Alki seep site, located approximately one mile south of Alki point, with bottom depth of ~160 meters. This was confirmed as our primary target site for the CAS test. We also found high concentrations in deep water (below 100 m) in the middle of the main basin (site 'P29') and near a sewage outfall site in Elliot Bay (site LSEP01). A site of gas seepage near Kingston showed significantly lower levels of methane concentration. It is likely that natural gas seeps and sewage outfall sites both produce high dissolved methane concentrations in the Puget Sound main basin below 100 m depth.

In the CAS CTD test cruise on June 8 and 9, 2021, we found good agreement between the in-situ methane concentrations using Niskin water samples analyzed on board ship by a second CAS and also analyzed by G.C. in our shore-based lab. A small difference between the lab GC results and the ship-board CAS results was improved with a revised extraction efficiency (determined by experiments on board NOAA ship Ron Brown in July) for our syringe GC method. A comparison between in-situ measurements and measurements of the head-space of returned water samples are shown in Figure 8. The measurements verified the basic "sea-worthiness" of the sensor, and demonstrated the ability to perform in-situ methane measurements.

- June 2021 – CTD from Rachael Carson
- Mounted on underside of Rosette
- Battery power
- Data streamed to deck via 2-wire connection
- In-situ methane concentration in water column at various depths
- Verified accuracy with returned sample measurements

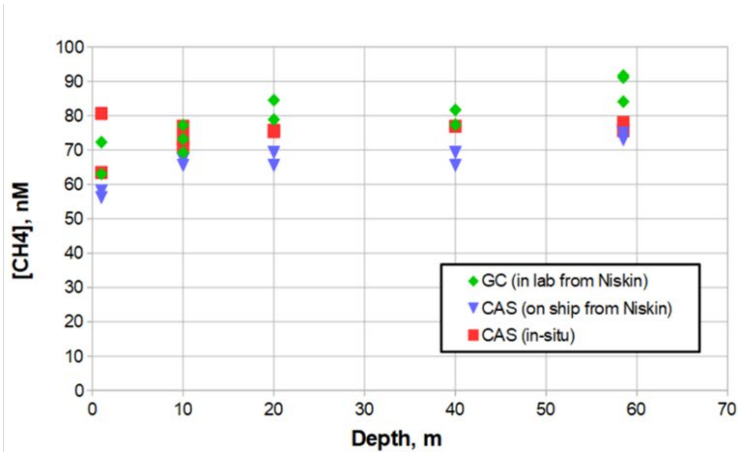

Figure 8. Comparison of in-situ CAS measurements from the CTD in Puget Sound as compared to analysis of returned samples. The bulleted text summarizes the results of the CTD test.

Another finding from the June 8/9 test cruise is that the device to transmit the ethernet signal over two wires through the CTD cable (approximately 2500 m long) has insufficient power. This was not indicated in the initial test done 6 months earlier. We adapted by using an available waterproof cable to transmit the Ethernet signal and handled that cable separately from the CTD cable. This limited our operational depth to <60 meters. This method could work to reach the bottom of Puget Sound but would not be feasible for depths > 250 meters. Another finding is that we need to have real-time feedback and control of the small McLane pump used to supply water to the CAS to know that it is running when the CAS is operating. The pump is not reliable enough to continue running through an entire CTD cast. We need better data communication than we currently have to operate the CAS reliably on a CTD, and we are considering how this can be accomplished.

In-situ methane measurements at vent sites taken with the CAS from an ROV dive in July 2022 are listed in Figure 9. These measurements are shown along-side off-line measurements of returned samples conducted with a GC. The system was demonstrated to accurately measure methane concentration with relatively high precision. In addition, the CAS enabled more measurements than was possible with the returned samples including additional samples at one location of interest ("Anemone"), as well as a measurement at an additional location ("Virgin Mound").

- July 2022 – ROV Jason
- Cruise cut short due to COVID
- 24V power from ROV
- Realtime data streamed to operator via ethernet connection
- In-situ methane concentration at vent sites down to ~ 1500 m
- Verified accuracy with returned sample measurements

Time of Sample	Vent Name	Methane Concentration	
		CAS In-Situ	GC post dive
18:55	205 – Anemone	8.66 µmol	
19.38	205 – Anemone		4.59 µmol
19:44	205 – Anemone	7.37 µmol	
20:17	205 – Anemone	7.10 µmol	
22:38	Inferno	54.5 µmol	
22:41	Inferno		51.0 µmol
00:59	205 – Anemone	7.15 µmol	
01:11	205 – Anemone	6.72 µmol	
02:40	205 – Anemone		4.99 µmol
03:32	Virgin Mound	125.4 µmol	
04:42	Hell		50.4 µmol
04:42	Hell		96.4 µmol
04:50	Hell	85.6 µmol	

Figure 9. Tabulated results of the CAS measurements during the ROV cruise at Axial Seamount, July 2022, as compared to returned samples.

Gas tight-samples collected during the ROV cruise were later analyzed at the Zurich isotope lab. Samples generally had an isotope composition of $\delta 13C = -25.0 \pm 0.7$ ‰. Only the samples analyzed from Virgin (collected in 2018 and 2020) showed a somewhat more negative carbon isotope composition of δ13C = -28.2 ± 0.2 ‰. Differences in the isotopic composition between these vents in the Ashes vent field, likely represent a higher input of microbial methane to the circulating fluid at Virgin.

2.4.2 Inventory of activities (number of submersible dives, CTD, net tows, etc.):

On March 31, 2021, we conducted 4 vertical CTD casts from the U.W. vessel Rachel Carson to investigate methane concentrations near sites of known or suspected gas seeps and near sewage outfall sites. Shipboard participants included David Butterfield, Matt Galaska, Sean McAllister, and Kevin Roe. We analyzed 44 water samples for methane concentration. Butterfield analyzed the samples in the lab at PMEL after the cruise. We also deployed a moored instrument (McLane PPS) for time-series DNA sampling near a known seep site.

On June 8 and 9, 2021, David Butterfield, Andrew Fahrland, Matt Galaska, and Kevin Roe conducted a test of the methane spectrometer on the U.W. vessel Rachel Carson in Puget Sound. Over two days, we conducted 4 CTD casts and collected 40 water samples for methane analysis. Dissolved methane concentration was analyzed by Tamara Baumberger in Marv Lilley's laboratory at U.W.

In July 2022, the system was utilized on the Jason ROV for one dive, deployed from the R/V Thompson. The following Operations log lists the primary activity for this cruise:

date UTC	time UTC	date/time local PST	Description	lat deg	lat min	lon deg	lon min	Z (m)
7/8/2022	16:30	7/8/2022 8:30	Depart Newport					
7/9/2022	15:00	7/9/2022 7:00	Arrive on station at Axial					
7/9/2022	15:32	7/9/2022 7:32	Jason dive J2-1434 at ASHES off deck	45	55.95	-130	0.7829	
7/10/2022	7:37	7/9/2022 23:37	Jason dive J2-1434 at ASHES on deck					
7/10/2022	8:08	7/10/2022 1:08	CTD at Ashes V22C-01	45	56.01	-130	0.788	1530
7/10/2022	13:00	7/10/2022 5:00	CTD at Ashes V22C-02 (no samples)	45	56.017	-130	0.794	1530
7/10/2022	19:06	7/10/2022 11:06	CTD at Ashes V22C-03	45	56.001	-130	0.788	1533
7/10/2022	23:41	7/10/2022 15:41	CTD at Ashes VC22C-04 (no samples)	45	56	-130	0.79	1507 ?
7/11/2022	0:43	7/10/2022 16:43	CTD at Int'l District VC22C-05	45	55.592	-129	58.751	1505
7/11/2022	8:05	7/11/2022 0:05	CTD background V22C-06	45	55.376	-129	56.507	1580
7/11/2022	11:41	7/11/2022 3:41	CTD Coquille V22C-07	45	55.031	-129	59.567	1521
7/11/2022	16:00	7/10/2022 8:00	Departed Axial and heading to Newport					
7/12/2022	21:00	7/12/2022 13:00	Arrived at Newport port					

2.4.3 Inventory of samples collected:

In July 2022, the system was utilized on the Jason ROV for one dive, deployed from the R/V Thompson. The following is a sampling list from that cruise.

Location	Sample	Comments	type	hr	min	sec	latitude	longitude	Z (m)
Anemone	J1434-HFS-1	Bag 16. **Failed**	fluid	18	39	2	45.933207	-130.01371	1540
Anemone	J1434-HFS-2	LV 9. Tmax=33.2C Tavg=30.5C Vol=8003ml. Methane measured 7.27 micromolar. Dense biota in area.	fluid	18	48	24	45.933207	-130.01371	1540
Anemone	J1434-HFS-3	Bag 17. Tmax=32.9C Tavg=32.3C Vol=553ml	fluid	19	33	2	45.933207	-130.01371	1540
Anemone	J1434-HFS-4	Bag 18. Tmax=32.6 C Tavg=31.7C Vol=551ml	fluid	19	37	4*	45.933207	-130.01371	1540
Anemone	J1434-GTHFS-5	Gastight on HFS intake. GT 2 w hite-blue	gas	19	44	44	45.933207	-130.01371	1540
Anemone	J1434-HFS-6	RNA filter 13. Tmax=34.3C Tavg=33.2C Vol=3195ml	fluid	19	47	37	45.933207	-130.01371	1540
Anemone	J1434-HFS-7	RNA filter 14. Tmax=34.7C Tavg=33.6C Vol=3003ml	fluid	20	921		45.933207	-130.01371	1540
Anemone	J1434-GTHFS-8	Gastight on HFS intake. GT 16 (8?) green-red	gas	20	21	34	45.933207	-130.01371	1540
Inferno	J1434-Geo-9	Sulfide chimney flange w ith biota. Some of it crumbled w hen placed in biobox. Screen position.	geo	22	15	31	45.93357	-130.0137	1537
Inferno	J1434-HFS-10	Piston 1. Tmax=231.1C; Tavg=221.8C Vol=540ml.	fluid	22	36	47	45.93357	-130.0137	1537
Inferno	J1434-HFS-11	Piston 2. Methane 54.5 micromolar; Tmax=235.2C; Tavg=228.6c; Vol=501ml.	fluid	22	41	25	45.93357	-130.0137	1537
Inferno	J1434-HFS-12	Piston 7. Approx. Time stamp. New screen position didn't move. Tmax=235.7C; Tavg=230.7c; Vol=501ml.	fluid	22	45	55	45.93357	-130.0137	1537
Inferno	J1434-GTB-13	Gastight bottle 9 red. Smaller chimlet temp w as 280C.	gas	23	9	33	45.93357	-130.0137	1537
Anemone	J1434-HFS-14	LV 10. Tmax=34.2C Tavg=32.9c Vol=8002ml. Position of previous Anemone samples.	fluid	0	59	30	45.933207	-130.01371	1540
Anemone	J1434-HFS-15	LV 11. Tmax=34.7C Tavg=33.1c Vol=8002ml	fluid	1	48	3	45.933207	-130.01371	1540
Anemone	J1434-HFS-16	Bag 19. Tmax=34.2C Tavg=33.7c Vol=552ml	fluid	2	33	45	45.933207	-130.01371	1540
Anemone	J1434-HFS-17	Bag 20. Tmax=34.3c Tavg=33.7c Vol=552ml	fluid	2	37	33	45.933207	-130.01371	1540
Virgin	J1434-HFS-18	Piston 3. Tmax=239C Tavg=198C Vol=311ml	fluid	3	21	37	45.933615	-130.01316	1539
Virgin	J1434-HFS-19	Piston 4. Tmax=220C Tavg=219C Vol=301ml	fluid	3	35	22	45.933615	-130.01316	1539
Virgin	J1434-GTB-20	Gastight bottle 10 orange blue	gas	3	45	15	45.933615	-130.01316	1539
Hell	J1434-HFS-21	Piston 5. Tmax=198C Tavg=184C Vol 501ml	fluid	4	43	1	45.93329	-130.01391	1538
Hell	J1434-HFS-22	Piston 6. Tmax=200C Tavg=193C Vol 502ml. Z differs from previous sample. Moved?	fluid	4	48	43	45.93329	-130.01391	1536
Hell	J1434-GTB-23	Gastight bottle 12 red yellow . Methane 85.6 micromolar. Fired tw ice.	gas	4	55	59	45.93329	-130.01391	1536
Hell	J1434-Geo-24	Flange near the base of Hell. Palm w orms also collected from the top of the flange. Successfully put in biobox.	geo bio	5	29	14	45.93329	-130.01391	1541
Hell	J1434-Bio-25	Suction in same area as previous sample near the base of Hell. Lots of limpets; scale w orms; palm w orms.	bio	5	33	3	45.93329	-130.01391	1541
Hell	J1434-Niskin-26	Niskin #2. 5m above top of Hell	fluid	5	45	20	45.93329	-130.01391	1532
Hell / Anemone	J1434-HFS-27	RNA filter 15. Tmax=2.9C Tavg=1.7C. Vol=3218ml. "Not discrete"? Betw een Hell and Anemone.	fluid	5	42	59	45.933151	-130.014	1532
~Anemone	J1434-Niskin-28	Niskin #1. 20m due S of Hell - Anemone area. Same altitude as previous Niskin? Looks like it. Jason log position: 45.922064; -130.013952	fluid	5	48	24	45.933044	-130.01391	1532
?	J1434-Niskin-29	Niskin #3. 100m to the south of Niskin #1. Location of miniSID release. Jason log position: 45.932612; -130.013716	fluid	6	6	51	45.93256	-130.01372	1540

2.4.4 Describe/list/append resulting publications, Web sites, presentations, etc.:

Publications:

- J. Kriesel, A. Fahrland, E. Ozen, I. Gat and J. Kelly, "Capillary Absorption Spectrometer (CAS), a compact, low-sample-volume isotope analyzer for planetary applications," 2023 IEEE Aerospace Conference, doi: 10.1109/AERO55745.2023.10115936
- J. Kriesel et al., "In-Situ, Real-Time Methane Sensor for Vents and Seeps," OCEANS 2023 - MTS/IEEE U.S. Gulf Coast, 2023, doi: 10.23919/OCEANS52994.2023.10337142.

Presentations:

- J. M. Kriesel, A. Fahrland, E. Ozen, and J. Kelly, "Mid-IR hollow fiber gas sensor applications in environmental sensing and isotope analysis," in Conference on Lasers and Electro-Optics, Technical Digest Series (Optica Publishing Group, 2022), paper AW4L.
- Jason M. Kriesel, Andrew Fahrland, "Methane isotope analysis: land, sea, and air", FACSS SciX conference, 2021.

Conference Poster:

- J. Kriesel, K. Emerson-Shurilla, A. Fahrland, E. Ozen, T. Baumberger, D.A. Butterfield "In-situ methane isotope analyzer testing at sites along the Mid-Atlantic ridge", American Geophysical Union (AGU) Fall Meeting, 2023.

Press release listed on multiple websites:
https://www.pmel.noaa.gov/news-story/successful-test-new-deep-sea-methane-spectrometer-coast-oregon
https://www.climate.gov/news-features/feed/successful-test-new-deep-sea-methane-spectrometer-coast-oregon
https://inergency.com/successful-test-of-a-new-deep-sea-methane-spectrometer-off-the-coast-of-oregon/

2.4.5 Location and status of data archive and/or sample storage, plan for public access, and final data inventory:

University of Washington and Oregon State University have stored samples. The samples will not be made available for public access.

2.4.6 Notation of major changes/adjustments to previously submitted documents:

None

3. Evaluation:

3.1 Accomplishments – Explain special problems, differences between scheduled and accomplished work:

While all of the primary objectives were accomplished, due to delays associated with the COVID pandemic, the schedule was extended beyond the originally planned effort.

3.2 Expenditures:

3.2.1 Describe original planned expenditures:

The planned expenditures were for system design, development, and testing. This included a mix of labor, parts, and indirect costs.

3.2.2 Describe actual expenditures:

The actual expenditures followed the plan to the most part with the exception that some of the funding was shifted from JPL and UW to OKSI as described below.

3.2.3 Include a final budget table with a column of original planned expenditures and a column of actual grant expenditures:

3.2.4 Explain special problems, differences between planned and actual expenditures:

Costs were shifted from JPL and UW to OKSI, due to the fact that OKSI took on additional work than was originally planned. In particular, work on the water sampling component planned for JPL, was done by OKSI. In addition, OKSI personnel participated in field collects, whereas the original plan did not include this participation.

3.3 Next Steps:

3.3.1 Planned or expected reports (professional papers, presentations, etc.)

None

3.3.2 Brief description of need for additional work, if any (next project phase, new research questions, unaccomplished work, etc.)

We have identified two separate paths in which the methane sensor can be improved:

- Improve the response time and size, weight, and power (SWaP) for AUV operations
- Improve the water sampling approach for accurate isotope ratio measurements.

To improve the response time and reduce the SwaP for AUV operation, we have engaged with a group at Woods Hole Oceanographic Institution (WHOI) led by Dr. Anna Michel. Together OKSI and the WHOI group collaborated on a NOAA SBIR proposal (submitted Dec. 2023) in which we plan to leverage the success of the CAS ROV system to develop an AUV version, see Figure 10.

As mentioned above, the isotope analysis of water samples was not sufficient to produce scientifically useful data. We believe this is due to isotope fractionation in the water sampling portion of the system. Since this was the first iteration of this concept, we believe that additional work on this aspect of the system could yield improved results, which would enable higher quality data.

Furthermore, OKSI's spin-off company, Guiding Photonics, has begun producing commercial products based on the methane sensing concept, see Figure 11. Improvement in the technology resulting from this effort can be directly inserted in furthering the sensor form, fit, and function for NOAA applications.

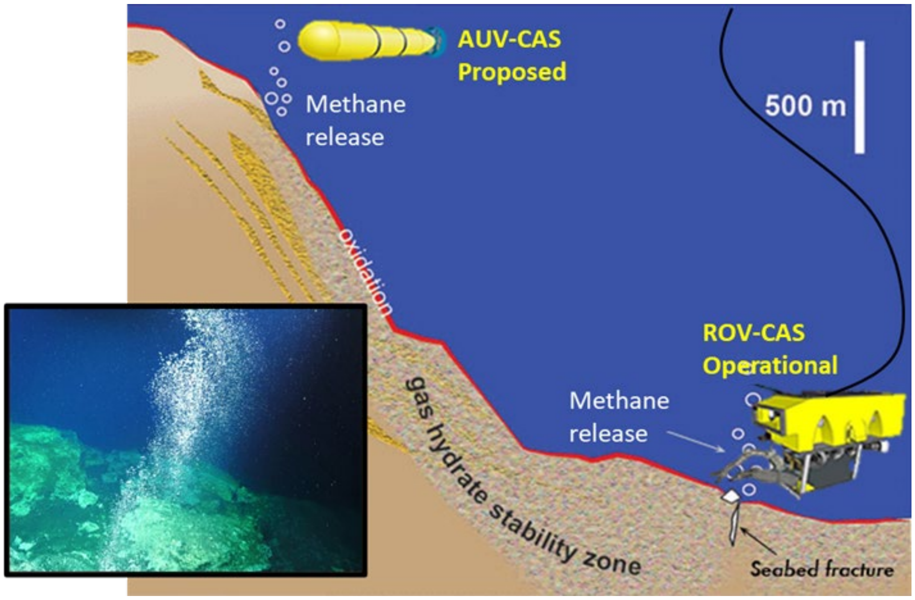

Figure 10. We propose to leverage our ROV-CAS to develop a new AUV-CAS. This new sensor will enable mapping and profiling of methane in the water column and trapped under ice to determine abundance and transport.

Figure 11. Picture of commercial methane sensor produced by OKSI’s spin-off company, Guiding Photonics.

Prepared By: ____ 2023-Dec-29

Signature of Principal Investigator Date