Developing In Situ Dissolved Inorganic Carbon Dioxide Instrumentation

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1. Introduction
The ocean carbon system plays a critical role in regulating carbon dioxide content in the atmosphere. With increased anthropogenic carbon input, it is even more important to understand the system through measurements, models, and predictions. Unfortunately, the spatiotemporal resolution of ocean carbon system measurements is limited by a lack of in situ instrumentation. The support of the Link Foundation Ocean Engineering and Instrumentation Fellowship has enabled me to make significant progress in developing an in situ carbon system instrument for the deep sea. The instrument will measure both total dissolved inorganic carbon (DIC) and the partial pressure of carbon dioxide (pCO₂), allowing for full parameterization of the carbon system. The main challenge of developing such an instrument is achieving the required precision (± 1 μmol/kg for DIC, ± 0.05 Pa for pCO₂) [1], while maintaining a reasonable time response (< 5 minutes) and deep-sea capability (> 1000 m). These specifications allow for detection of changes in biogeochemical cycles and ocean acidification with sufficient spatial resolution during surveys [1-5]. This precision can be achieved by pairing tunable laser diode absorption spectroscopy (TLDAS), which has excellent field precision in atmospheric chemistry applications [6-8], with a deep-sea membrane interface [9,10]. The primary technical challenges are expanding TLDAS to cover an increased concentration range, quantifying the dynamic effects of the membrane interface, and designing a highly multidisciplinary integrated system for variable field conditions. With this instrument, scientists will have unprecedented access to high resolution, high precision carbon system measurements in the deep sea, opening many future avenues of inquiry.

2. Results
With the support of the Link Foundation, I have made advances in three major development areas: 1) membrane inlet design, 2) precision laser spectroscopy, and 3) complex systems development. In addition to laboratory and analytical work, I conducted field-testing for two subsystems: a prototype total dissolved gas pressure (TDGP) sensor and a prototype pCO₂ sensor. In this section I will overview the carbon system instrument measurement process, and then report on field test results.

System Overview:
Figure 1 shows a system diagram overviewing the major subsystems of the instrument. Measurements of DIC and pCO₂ are completed as follows:

1. Seawater is pumped past the membrane inlet. If DIC is being measured, the seawater is acidified to drive the carbonate system equilibrium towards gaseous CO₂. Meanwhile, the TDGP of the flow is monitored.
2. Gas is extracted from the flow via a membrane inlet. The gas fills a multipass optical cell held at vacuum. The same optical cell may be used for both pCO₂ and DIC measurements because of the large dynamic range of TLDAS.

3. The concentration of the gas (xCO₂) is measured in the optical cell via TLDAS. The laser tunes across an absorption line of CO₂ at 2.004 μm, and the attenuation of light is monitored. Onboard processing infers xCO₂ from the measured absorption profile via a nonlinear curve fit. DIC or pCO₂ can then be calculated using Dalton’s and Henry’s laws:

\[ pCO₂ = xCO₂ \cdot TDGP \]  
\[ DIC = kH \cdot xCO₂ \cdot TDGP \]  

**Figure 1:** System Diagram. Measurements of DIC and pCO₂ are conducted by alternating between acidified and unmodified seawater flow. Gas is extracted via a membrane inlet, and the TDGP is monitored. Inside the deep-sea housing, TDLAS is used to measure the CO₂ concentration in the extracted gas. For long term deployments, gas is removed from the instrument via a membrane outlet, to avoid pressurizing the housing. Data is collected and processed autonomously via onboard electronics.

**Membrane Inlet Design – TDGP Sensor and pCO₂ Inlet Testing:**
I designed a low cost, self-powered, autonomous, self-logging total dissolved gas pressure sensor (TDGP) for use up to 1000 m, shown Figure 2. It has 4 membrane interfaces to allow testing of different membrane configurations or simultaneous comparison of low cost sensors. The TDGP works by monitoring the absolute pressure of a small headspace behind a membrane interface. I conducted field tests of the TDGP using the ROV Subbastian on the R/V Falkor to a maximum depth of 775m at Cascadia Margin methane seeps, off the coast of Oregon. All mechanical and electrical systems were successful. A high factor of safety was used in the mechanical design of the membrane interface to reduce the risk of membrane failure. The tradeoff for reduced risk was increased membrane equilibration time. The next generation mechanical design of the TDGP had a significantly improved time response on a summer 2019 test in a shipboard flow-through system aboard the R/V Thomas G. Thompson off the coast of New Jersey. Future work remains
to optimize the membrane interface for time response in the deep sea. Figure 3 shows data from both first and second-generation designs, as well as data from a Pro-Oceanus TDGP instrument.

I used the second-generation membrane interface for extracting gas from seawater for the prototype pCO₂ instrument, also tested on the summer 2019 cruise. Instead of passively equilibrating gas into a small headspace, a vacuum (at 2 kPa absolute pressure) is used to pull gas into the instrument. Three other membrane interfaces monitored TDGP, which equilibrates passively. This setup allowed me to compare the response of the membrane interface under active and passive equilibration conditions in varying field conditions. Understanding the equilibration of gasses across the membrane interface is critical for instrument development and ensuring final system accuracy.

Figure 2: Prototype TDGP sensor, capable of 1000 m deployment. Four membrane interfaces allow comparison of identical low cost sensors or comparison of different membrane configurations. Shown on a Woods Hole, MA dock.

Figure 3: A time series of TDGP data from the first and second-generation membrane inlet designs, with comparison to a commercial TDGP sensor from Pro-Oceanus. Data is from a summer 2019 cruise aboard the R/V Thomas G. Thompson. A significant improvement in time response from TDGP version 1 to TDGP version 2 was observed. A Hampel filter was used to eliminate spurious spikes from the Pro-Oceanus data.
Precision Laser Spectroscopy and Systems Development – pCO2 Instrument Testing:
To synthesize both analytical and experimental work towards developing a laser spectroscopy based carbon system instrument, I built a prototype pCO2 instrument for shipboard use. With the exception of acidification, the physical systems for DIC and pCO2 are nearly identical, so it was most efficient to test pCO2 first. The final design will be deep-sea capable, however keeping the system in a surface version for the initial prototypes reduces complexity and allows for rapid iteration. The pCO2 instrument uses TDLAS to measure the concentration of CO2 extracted from seawater via a membrane inlet. The instrument autonomously collects and displays data in real-time on the instrument control interface. Gas pressure and temperature is monitored and used for concentration calculations. Nonlinear curve fitting is used to extract the gas concentration from the raw laser tuning data, and the background signal is removed online, eliminating reliance on alternating purging the cell with N2 and sample measurement. This reduces consumables, which is necessary for future deep-sea designs. Additionally, the instrument was built into a Pelican case for transport and is watertight for future deployment on mobile platforms.

The pCO2 instrument was tested on the R/V Thomas G. Thompson on the shipboard flow-through system, shown in Figure 4. A pCO2 instrument from NOAA/PMEL was monitoring the same flow, allowing for comparison between the different sensor modalities. Data from that comparison instrument are forthcoming. I also helped to develop low-cost multi-gas sensor suite for CO2, O2, and TDGP using off the shelf sensors. Using my 4-part membrane interface design, I tested 3 multi-gas sensor suites. The data from the pCO2 instrument demonstrates good correspondence with the low cost sensors. The CO2 calibration curve and Allan deviation for the laser spectrometer are shown in Figure 5. Allan deviation is used in laser spectroscopy to estimate the precision of a laser spectrometer, and more accurately accounts for the 1/f noise present in laser systems. The spectrometer showed a linear response and an ultimate precision of 0.65 ppm. This result indicates that at 1 bar TDGP, the precision of the instrument is ± 0.065 Pa. The target precision is ± 0.05 Pa, which should be possible to meet with minor refinements. Further testing with certified reference materials will be required to validate the instrument’s accuracy.

Figure 4: Prototype flow-through pCO2 instrument. Left: general overview of instrument internals. A livestream of data is shown on the control interface. Right: pCO2 sensor aboard the R/V Thomas G. Thompson on summer 2019 cruise.
Figure 5: Prototype pCO$_2$ instrument calibration curve and Allan deviation, showing the linear response and ultimate precision of the instrument. Allan deviation is used in laser spectroscopy to determine the precision of a measurement. Concentration is calculated first through a nonlinear curve fit on the laser tuning data and then corrected using the calibration curve to improve accuracy, here shown using the absorbance area to compare measurements.

3. Significance and Impact:
Developing the pCO$_2$ instrument required a multidisciplinary and complex system design, using skills from the fields of mechanics, optics, electronics, software, statistics, ocean engineering and chemistry. Overcoming the design hurdles involved represents a significant step towards
developing a combined DIC and pCO₂ instrument for the deep sea. The shipboard precision of
the laser spectrometer was close to the required pCO₂ measurement precision, indicating that this
methodology warrants further development into a combined DIC/pCO₂ instrument.

In the context of broader scientific objectives, development of a precision \textit{in situ} carbon
system instrument will facilitate scientific inquiry beyond bottle samples. By increasing the
spatiotemporal resolution and vastly increasing measurement count, an \textit{in situ} instrument can
reveal phenomena previously impossible or prohibitively expensive to study. Potential
applications include studying the small-scale variations in the carbon system near cold-water
coral habitats, detecting long-term changes due to ocean acidification on an ocean observatory,
or mapping the carbon system near deep-sea vents.

4. Future Prospects:
The next course of development includes synthesizing results from the pCO₂ sensor deployment
and making design changes to improve the design, in addition to implementing acidification and
adapting the design for packaging into a deep-sea pressure housing. I will continue development
towards a dual DIC/pCO₂ instrument through laboratory experiments, design work, and
continued field-testing. Upon completion of this project, I will demonstrate the carbon system
instrument on a cruise to Guaymas Basin to observe hydrothermal vent systems. In the future I
will find ways to enable other scientists to use the technology, either through collaboration with
instrument manufacturers or open sourcing.

5. Scholarly Reports
An abstract on the pCO₂ instrument development and results will be submitted to Ocean
Sciences 2020. After further development work, the carbon system instrument for pCO₂ and DIC
will be published in appropriate academic journals.

6. Fellowship Impact
This fellowship funding supported my doctoral thesis work in ocean instrumentation. It provided
me with critically important funding which allowed me to develop better prototype pCO₂ and
TDGP instrumentation. This supports the overall goal of my thesis to develop an \textit{in situ} deep-sea
carbon system instrument with sufficient precision, time response, and depth capability, in order
to expand the tools available for scientific inquiry.

7. References:

System Variables," in Proceedings of OceanObs’09: Sustained Ocean Observations and


