DOEI: Toward In-situ Measurements of the CO_2 System in Deep Ocean

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The marine CO_2 (carbonate) system, often defined by four primary parameters [pH, pCO_2, total dissolved inorganic carbon (DIC), and total alkalinity (TA)], plays a critical role in regulating the capacity of the world's oceans to absorb CO_2 from the atmosphere. Study of this system is central to predicting impacts of future climate change and ocean acidification. This fundamentally relies on high quality measurements of the marine CO_2 system at appropriate temporal and spatial scales.

There is an increasing demand for in-situ measurements of the CO_2 system, via observation networks consisting of various platforms, such as buoys, Remotely Operated Vehicles (ROVs), and Autonomous Underwater Vehicles (AUVs). At least two of the four CO_2 parameters are required to fully characterize the system. However, simultaneous in-situ measurements of multiple CO_2 parameters have just begun to emerge. Our ability to study the CO_2 system as a whole is still limited. We still largely rely on shipboard bottle sampling and discrete analyses of the four CO_2 parameters to cover all depths in the ocean. Advancing and enabling ocean technologies (e.g. sensors and platforms), especially those with sub-surface and deep ocean capabilities, has been one of the highest research priorities in ocean science.

The goal of this study was to initialize development of an in-situ, spectrophotometric pH plus DIC sensor package with full water-depth mapping capability that can be deployed on ROVs, AUVs, and in-situ profilers. DIC is a measure of the total concentrations of carbonate species, including dissolved CO_2, carbonic acid, bicarbonate and carbonate ions; while pH is a measure of hydrogen ion concentration or acidity. They are important parameters that oceanographers use to describe and quantify many biogeochemical processes in the ocean, such as biological activity by primary producers (phytoplankton) and air-sea CO_2 exchange. How well and how fast we can measure these parameters ultimately determines our capability of characterizing these important processes in the ocean. Currently, there is no existing

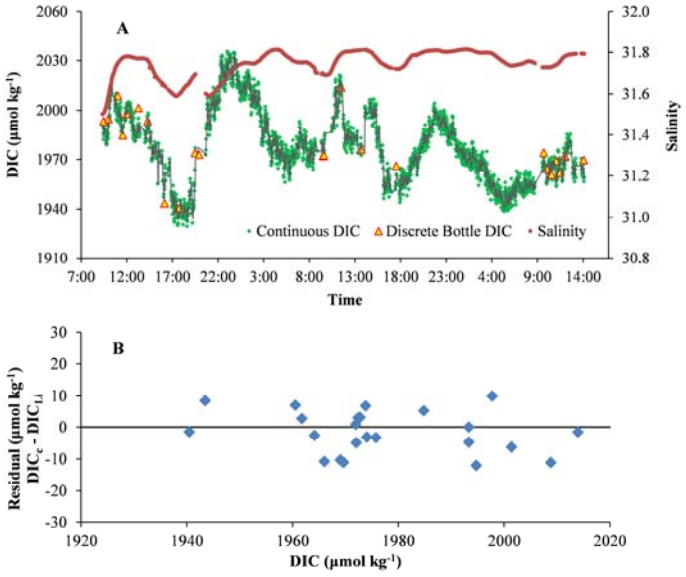

Fig. 1. (A) Continuous, spectrophotometric DIC measurements of flow-through seawater at the WHOI Environmental System Lab using the newly developed DIC method, along with salinity data and traditional bottle DIC measurements. The measurement frequency of the continuous DIC method is 1 Hz. The data were binned to one minute interval. (B) Residual plot between continuous DIC and bottle DIC measurements, showing a mean difference of -1.6 ± 6.7 µmol kg^{-1} (N = 23).

in-situ sensor that can achieve simultaneous measurements of multiple CO_2 parameters on mobile platforms.

Through the support of this project, we have developed a new spectrophotometric method for high-resolution DIC measurements (Fig. 1) that is suitable for submerged, in-situ applications, particularly targeted for mobile platforms, such as ROVs and AUVs. We also improved spectrophotometric pH measurements by mixing pH indicator and seawater sample in a re-circulating fashion. As such, we improved signal-to-noise ratio and reduced reagent consumption, two desirable features for in-situ applications. These advancements open the door to simultaneous, in-situ measurements of pH and DIC and complete characterization of the seawater CO_2 system in high-resolution in the deep ocean.

The new DIC method features a fast response time of ~22s, which improves the spatiotemporal resolution by more than one order of magnitude compared to the existing spectrophotometric method. The flow-through equilibration allows for continuous (~1 Hz) detection and real-time data smoothing. The new DIC method shows a precision of ±3.6 µmol kg^{-1} (N = 2332) during a series of lab and field testing (Figs. 1 and 2). The accuracy of the method was evaluated by comparing its measurements with traditional bottle measurements. The agreements between the two, as shown in Figs. 1 and 2, are ±6.0–6.7 µmol kg^{-1}. This level of precision and accuracy is comparable to that of the existing spectrophotometric method. The characteristics of the new method make it particularly suitable for high-frequency, submerged measurements required for mobile observing platforms in the ocean.

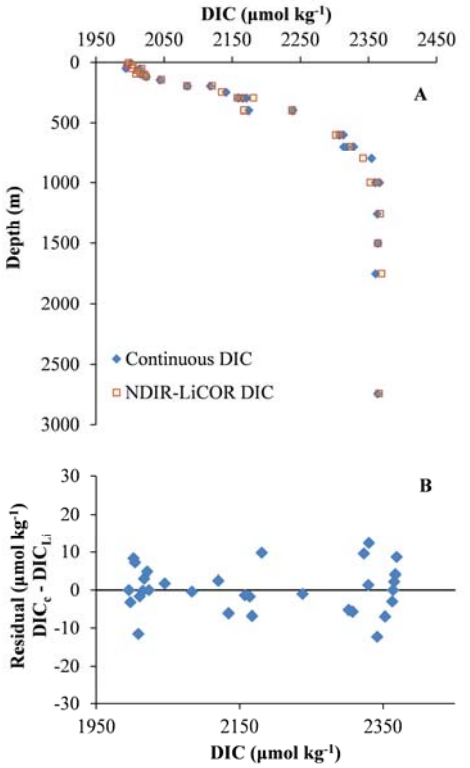

Fig. 2. (A) Comparison of the water-column DIC profiles between the measurements made by the new DIC method and the NDIR-based method over discrete bottle samples collected in the North Pacific in September 2012; (B) Residuals between the two measurements.

By using re-circulation during the mixing between seawater sample and pH indicator, the signal-to-noise ratio for the spectrophotometric pH measurements was improved by ~30%. In addition, pH indicator and seawater consumption during one measurement cycle was reduced by > 50%. The measurement precision was evaluated to be better than 0.001 pH units, which are comparable to measurements by a high-precision bench-top system.

The new DIC method and the improved pH method are being adopted on a buoy-based in-situ sensor package for real-time measurements of the seawater CO_2 system (Fig. 3). The sensor package is currently under testing. It is among the first of the in-situ carbon sensors that simultaneously measure two of the four CO_2 primary parameters. As such, the CO_2 system can be completely defined by thermodynamic calculations. In addition, the pH-DIC pair

is desirable in such calculations as it will produce less calculation errors. In terms of measurement frequency, this sensor package is the fastest among the existing DIC and pH sensors.

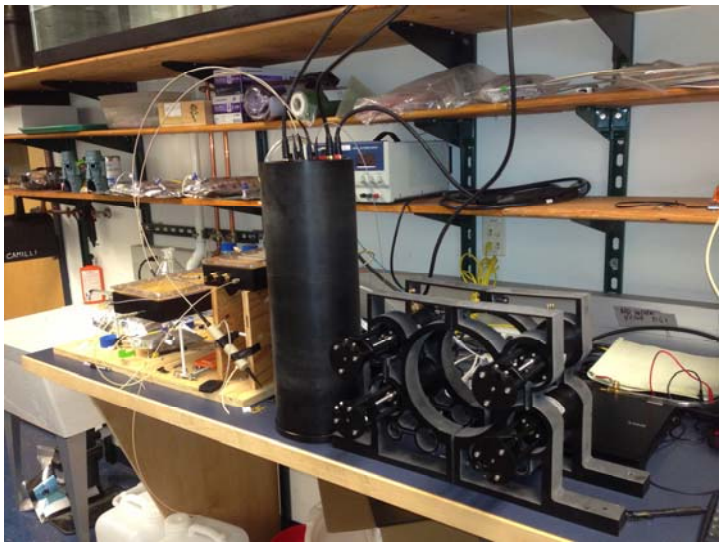

Fig. 3. A buoy-based in-situ DIC and pH sensor package.

In order to apply the new spectrophotometric DIC method for deep ocean operation, a custom-build optical-pressure cell was built to calibrate molecular properties of indicators as functions of pressure to be encountered in field deployment. For spectrophotometric pH measurements, pressure effects of indicators have been previously determined. We will determine pressure effects of other indicators next to cover more pH and DIC ranges encountered in the ocean.

Using valuable data obtained through this study, we have recently secured National Science Foundation funding to develop an in-situ sensor for continuous seawater DIC measurements based on the new flow-through method. The new sensor will be deployed on AUVs/ROVs and water-column profiling with an operational depth up to a few thousand meters in the ocean. This will greatly improve our capability to study ocean chemistry, ocean acidification, and ocean carbon cycle.