Prospects for autonomous inorganic carbon measurements

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Introduction

Inorganic carbon parameters are commonly measured as part of oceanic carbon cycle studies. The four measurable CO_2 parameters are total CO_2 (TCO_2), total alkalinity (TA), total hydrogen ion concentration (pH_T) and partial pressure of CO_2 (pCO_2). All four CO_2 parameters can be measured on ships with excellent accuracy and precision. The dissolved inorganic carbon equilibria are constrained by measurement of two of these parameters. For example, if TCO_2 and pH_T are known, pCO_2, TA, CO_2(aq), H_2CO_3, HCO_3^-, CO_3^{2-} and $CaCO_3$ saturation can be calculated. The objective of most studies is to quantify TA and TCO_2. Air-sea CO_2 flux calculations also require sea surface pCO_2 (e.g. Takahashi et al. 1997). Because pCO_2 is highly variable and not well-understood, it is often measured in carbon process studies (e.g. Oudot 1989; Robertson et al. 1993; Boyd et al. 2000). Depth-resolved TCO_2 measurements are used to quantify inorganic carbon budgets in the water column. Time-series of TCO_2 in the euphotic zone give important insights into the biological and physical mechanisms that control carbon fluxes (e.g. Chipman et al. 1993; Marchal et al. 1996: Gruber et al. 1999). Full water column TCO_2 inventories are being used to quantify the uptake of anthropogenic CO_2 (Gruber et al. 1996; Peng et al. 1998; Körtzinger et al. 1998).

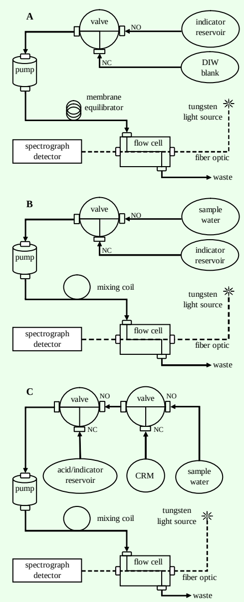
A major initiative of oceanographic programs such as GOOS is to develop these measurements for autonomous characterization of the ocean carbon cycle. At present, only autonomous pCO_2 systems are fairly well-advanced (e.g. Friederich et al. 1995; Hood et al. 1999; DeGrandpre et al. 1995). Less progress has been made on the other inorganic carbon parameters. TCO_2 is probably the most technically challenging measurement because of the need for acidification and quantification of the liberated CO_2. Alternatively, TCO_2 can be calculated from measurements of pH_T and TA, or pCO_2 and TA (the pH-pCO_2 combination is prone to large TCO_2 errors, see Millero et al. 1993).

Figure 1: The SAMI-CO_2 in its mooring cage. The SAMI is a membrane-based sensor that measures the partial pressure of CO_2. It can operate for up to 1 year with a ~24/day measurement frequency. The instrument was developed for mooring applications but could easily be made more compact for smaller payload platforms.

Our past research has focused on the development of a CO_2 sensor named the submersible autonomous moored instrument for CO_2 (SAMI-CO_2) (DeGrandpre et al. 1995) (Figure 1). These sensors are now commercially available from Sunburst Sensors, LLC in Missoula, Montana. One of our present goals is to adapt this technology for pH_T and TA measurements for full characterization of inorganic carbon (Figure 2). The new sensors are named SAMI-pH and SAMI-alk because their designs derive directly from SAMI-CO_2.

Methods

Figure 1: Schematic diagrams of (A) SAMI-CO_2, (B) SAMI-pH and (C) SAMI-alk. Because all three analytical systems are based on spectrophotometric pH measurements, the designs use the same pump and valve configuration and optical detection schemes. SAMI-CO_2 does not actually sample the ambient seawater but uses a membrane to equilibrate with seawater pCO_2 (A). To perform pH_T measurements (B), the membrane is replaced with a mixing coil. The indicator is relocated to the normally-closed (NC) port of the 3-way valve and seawater is drawn through the normally-open (NO) port. The pH_T configuration is adapted for total alkalinity measurements by simply replacing the pure indicator solution with a HCl/indicator mixture. An additional 3-way valve is used to introduce an alkalinity Certified Reference Material (Dickson et al. 2003).

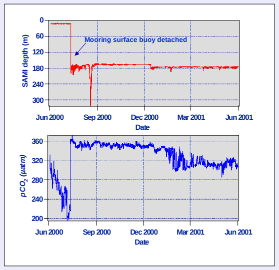


State of the Technology

SAMI-CO_2 (Figure 2A)

The SAMI-CO_2 is a well understood and proven technology that has been widely used in many marine field studies. These studies have been undertaken by our group and by a number of international collaborators. Deployments have been made on drifters and moorings in all of the world's oceans. SAMIs are currently deployed in the Beaufort Sea, the eastern North Atlantic (PAP time-series), western North Atlantic (CIS time-series), and eastern North Pacific (PAPA time-series). Results from a 1 year deployment in the Labrador Sea are shown in Figure 3.

Figure 3: 12 months of continuous SAMI-CO_2 data collected in the Labrador Sea (the surface flotation parted and the mooring sank to 180 m depth). Excellent long-term stability is apparent during the ~6 month period prior to winter deep convection (late January). However, no shipboard pCO_2 data were available at 180 m depth for validation of the pCO_2 data. During the latter half of the time-series, the SAMI-CO_2 was within the pycnocline creating a strong correlation between pCO_2 and temperature (not shown) (data were collected in collaboration with D. Wallace and U. Send, IfM, Kiel, Germany).



SAMI-pH (Figure 2B)

A prototype SAMI-pH instrument has been developed and tested for freshwater applications (Martz et al. 2003). The instrument is essentially identical in appearance to SAMI-CO_2 (Figure 1). An 8-day time-series is presented in Figure 4.

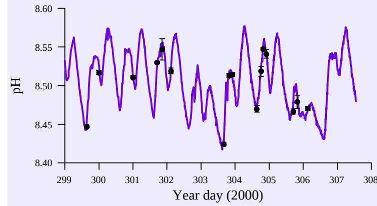


Figure 4: In situ SAMI-pH measurements (purple line) in the Clark Fork River. Lab spectrophotometric measurements are also shown (black circles).

SAMI-pH can be readily adapted for seawater pH measurements. Autonomous pH_T may have significant advantages over pCO_2 for inorganic carbon characterization on Lagrangian platform including a faster response time and potentially better reliability because pre-deployment gas phase (CO_2) calibrations are not required.

SAMI-alk (Figure 2C)

SAMI-alk is the least well-advanced of the three systems. We have recently obtained preliminary data demonstrating the feasibility of using the design in Figure 2C and a theoretical model has been developed to predict the sensor response. We are currently seeking grant support from NSF for continuation of this work.

Summary

A sensor combination that measures pCO_2 or pH_T with total alkalinity can be used to quantify TCO_2 and thereby provide very valuable information for understanding the mechanisms that control CO_2 exchange between the oceans and atmosphere. Developing this combination of sensors with sufficient precision and accuracy is feasible but will require a diligent, single-minded, bull-headed, long-term effort with an equal long-term commitment and patience by funding agencies. After all, conductivity sensors weren't developed overnight!

More background information:

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Acknowledgments

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