IMBER is an international project that aims to investigate the sensitivity of marine biogeochemical cycles and ecosystems to global change, on time scales ranging from years to decades. IMBER aims to provide a comprehensive understanding of, and accurate predictive capacity for ocean responses to accelerating global change and the consequent effects on the Earth System and human society.


### 2.2 Observing changes in the surface ocean carbon inventory, autonomously

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The ocean exerts significant influence on global climate through carbon cycle feedback mechanisms that affect the air-sea exchange of carbon dioxide (CO₂) gas (Passow and Carlson, 2012; Ciais et al., 2013). Many of these feedback mechanisms are influenced by biological processes for which preindustrial baseline information does not exist. Thus, in a climate now transitioning away from preindustrial equilibrium, biogeochemical feedbacks may be even more challenging to discern and quantify.

In recognition of this issue, an immense effort has gone into the quantitative characterization of marine carbon cycling and biological carbon export from the surface ocean over the past few decades (e.g., Emerson, 2014). In particular, numerous investigators have worked to advance the technology available for autonomous carbon cycle studies (Johnson et al., 2009; Schuster et al., 2009) to learn more about the interplay of thermodynamic and biogeochemical controls on the observed global air-sea CO₂ exchange. The marine inorganic carbon system is often described by four primary parameters: dissolved inorganic carbon (DIC), total alkalinity (TA), CO₂, and pH. DIC is the sum of dissolved molecular species derived from CO₂. TA is a measure of the seawater charge balance. Measurement of any two of these four parameters, in addition to salinity and temperature, can be used to calculate all of the other carbonate system parameters (Millero, 2007) and to quantitatively evaluate the drivers of marine carbon cycling. In the past 10 years, autonomous CO₂ and pH sensors have become commercially available for moorings enabling the collection of high-frequency (<daily) time series observations of the carbonate system (Sutton et al., 2014).
Unfortunately, CO₂ and pH are the least ideal pair to constrain the carbonate system due to their strong covariance. Uncoupling of the CO₂ and pH uncertainties leads to large errors in the calculations of DIC and TA (>100 µmol kg⁻¹) (Dickson and Riley, 1978; Cullison Gray et al., 2011). Recognizing the challenges associated with further improving autonomous CO₂ and pH sensor measurement accuracies (~1 µatm and ~0.003, respectively), we set out to develop an autonomous surface ocean DIC sensor for moored application.

The Moored Autonomous DIC (MADIC) sensor was modified from the Pacific Marine Environmental Laboratory MAPCO₂ system design (Fig. 8, Sutton et al., 2014). A 10-port valve with fixed-volume tubing loops is used to collect calibrated volumes of seawater (~1 mL) from ~1m depth, and of acid (~200 µL) from an acid reservoir within the equilibrator tube. The acid and seawater mix inside an equilibration chamber as initially CO₂-free air is bubbled through the acidic sample in a closed loop until equilibrium is reached. Most of the DIC in the acidic solution is transferred to the gas phase, and at equilibrium, CO₂ in the gas phase is measured with an infrared detector. The DIC concentration of the seawater is determined from the CO₂ content, pressure and temperature of the gas phase at equilibrium, measurements of sea water salinity and temperature from an external CTD at the time of sample injection, the Ideal Gas Law, and Henry’s Law (Fassbender et al., 2015). Each measurement takes ~12 minutes to complete, including satellite transmission of the data after every two samples. The laboratory determined accuracy was found to be ±5 µmol kg⁻¹.

After rigorous testing in the laboratory and at the Seattle Aquarium, the MADIC sensor was deployed near Honolulu, Hawaii for a fully autonomous field test from November 2013 to May 2014. The sensor was mounted on a moored buoy with a Seabird Electronics CTD and SAMI² pH sensor affixed to the bridle and was positioned ~400m from shore and ~25m from another buoy carrying a MAPCO₂ sensor. Fifty two discrete samples were collected throughout the deployment and analyzed for DIC via coulometry at the University of Hawaii SOEST Laboratory. Results indicate that the MADIC sensor measurements were ~90% more...
accurate than DIC values calculated from in situ measurements of pH and CO₂, based on the 52 high-quality discrete DIC samples that were collected (Fig. 9, Fassbender et al., 2015).

The MADIC system is a first step toward autonomous and continuous monitoring of the surface ocean carbon inventory. Near real-time data transmission and remote control of the sensor through two-way satellite communication makes it possible to increase the sample frequency (up to 4 samples per hour) during interesting or intermittent environmental events. In addition, the sample injection volume can be altered so that a wider range of DIC concentrations than those observed in the surface ocean can be measured. The utility of the MADIC analyzer for long-term observing is particularly apparent in nearshore and high-latitude regions where fresh water input can lead to environmental conditions outside of the charge balance assumptions used to define ocean pH and TA (Dickson, 1981, 1984). In these environments, the direct measurement of DIC may be essential for robust constraint of the carbonate system until charge balance definitions are expanded.

The next phase in advancing autonomous marine carbon cycle observing capabilities will be the combination of two carbonate system sensors in one package, such that one platform can house multiple sensors and over constrain the carbonate system. The development of dual carbonate system sensors is well underway (Wang et al., 2015) and sensors for a variety of monitoring platforms and applications have proliferated over the past 5 years (for example: Martz et al., 2010; Easley et al., 2013; Li et al., 2013; Liu et al., 2013; Spaulding et al., 2014). Commercialization of these sensors coupled with continued technology advancement in the coming years will provide a wealth of new research opportunities for the broader carbon research community.

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