Creating Controlled CO_2 Perturbation Experiments on the Seafloor – Development of FOCE Techniques

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***Abstract* - We report recent progress on the design and testing of systems for carrying out controlled CO_2 perturbation experiments on the sea floor with the goal of simulating the conditions of a future high CO_2 world. Controlled CO_2 enrichment (FACE) experiments have long been carried out on land to investigate the effects of elevated atmospheric CO_2 levels on vegetation, but only limited work on CO_2 enrichment on enclosed systems has yet been carried out in the ocean. With rising concern over the impacts of ocean acidification on marine life there is a need for greatly improved techniques for carrying out in situ experiments, which can create a ΔpH of 0.3 to 0.5 by addition of CO_2, on natural ecosystems such as coral reefs, cold water corals, and other sensitive benthic habitats.**

This is no easy task. Unlike land based experiments where simple mixing in air is all that is required, CO_2 has complex chemistry in seawater with significantly slow reaction kinetics. Scientists must design systems to take this into account. The net result of adding a small quantity of CO_2 to sea water is to reduce the concentration of dissolved carbonate ion, and increase bicarbonate ion through the following reaction:

$$CO_2 + H_2O + CO_3^{2-} \rightarrow 2HCO_3^-$$

In practice the reaction between CO_2 and H_2O is slow and is a complex function of temperature, pH, and TCO_2, with the reaction proceeding more rapidly at lower pH and higher temperatures. Marine animals in the natural ocean will typically experience only small and temporary shifts from environmental CO_2 equilibrium. Valid perturbation experiments must try to expose an experimental region to a stable lower pH condition, and avoid large and rapid pH variability.

The most common sensor used for experimental control is the pH electrode, and this detects only H^+ ion, not any of the dissolved CO_2 species. We first explored the reaction kinetics of a CO_2 perturbation in a series of closed loop pH cell experiments carried out at various depths under ROV control. These were found to be well matched to the Zeebe & Wolf-Gladrow [1] model. From these results, functions for the delay time required for equilibrium were devised and a design for a delay loop to achieve at least 2 e-folding times between CO_2 injection and animal exposure was developed.

We tested this prototype system in October 2007 in a series of ROV controlled experiments at a depth of 1000 meters. The working fluid used for enrichment was surface sea water saturated at one atmosphere with pure CO_2 gas to create a solution of about pH 4.8 and 56 mM total CO_2. This was carried to depth in a 56 liter piston accumulator, and dispensed as needed into a flexible polyethylene bag for subsequent addition into the experimental unit.

The design consisted of a 4 meter delay loop leading to a control volume (square box, 25 cm per side) outfitted with three pH electrodes and a CTD. To determine the uniformity of the pH, two pH electrodes were positioned in the control volume and a third electrode was positioned just beyond the control volume in the flow stream. Ambient seawater, pumped at a desired rate with a modified thruster, was mixed at the beginning of the delay loop with controlled continuous injection of the CO_2-rich working fluid in a ratio typically of about 200:1 depending on the pH perturbation desired.

For these initial tests, a feed-forward system was used where flow rates of both the ambient seawater and CO_2-rich seawater were varied to produce a desired pH change. Future designs will incorporate a feedback loop to allow for automated precision pH control.

These field tests were successful in showing that a plume of lower pH seawater could be accurately created and maintained in the deep ocean. The pH was reduced by up to 0.9 pH units from the ambient value of 7.8 covering well beyond the range of projected ocean pH scenarios for the next century. Near future goals will involve use of the MARS undersea cable recently deployed in Monterey Bay, California for power, communication and control, and a long-term experiment will be performed to demonstrate the operational feasibility of this technology for ocean acidification studies worldwide.

I. INTRODUCTION

Scientists at the Monterey Bay Aquarium Research Institute (MBARI) have undertaken a series of small-scale in-situ CO_2 enrichment experiments in order to simulate the present and predicted future effects of fossil fuel CO_2 emissions on ocean pH. In excess of 25 gigatons CO_2 are added to the atmosphere each year and the ocean has been the primary sink of these emissions. Presently, the ocean is absorbing on average 1 million tons of fossil fuel CO_2 per hour. The result of this process has been a lowering of the surface ocean pH by approximately 0.1 units during the past 100 years. Recent geochemical models project an additional drop of 0.2 units by the middle of this century.

Terrestrial FACE (Free Air Carbon Dioxide Enrichment) experiments have been implemented for long term studies and are considered a worthwhile multi-discipline approach to global CO_2 research. Presently there are only a few oceanic facilities that have attempted to examine the pH changes that global ocean ecosystems are expected to experience in the coming decades, and none have employed the FACE approach. Over the past three years, MBARI has used their extensive background in CO_2 research to develop a prototype oceanic system based on the scientifically accepted concepts of the terrestrial FACE experiments (Fig. 1). Our initial effort

Figure 1. Prototype FOCE system deployment

has led to two deployments of a small system that allows real time feedback and modulation of pH in a small control volume [2]. The prototype system imitated projected pH changes due to rising levels of CO_2 using a low concentration mixture of HCl released into the ocean environment.

Our initial deployments demonstrated the functional engineering elements but also highlighted some fundamental problems related to the slow reaction kinetics of CO_2 in seawater. The time delay for complete mixing of the pH altering fluid with ambient seawater was on the order of minutes. Considering average bottom currents of approximately 5-10 cm/sec, we would need to release our pH altering fluid 20 to 30 meters away from our control volume to get complete pH equilibrium. It was determined to be too difficult to design a seafloor system that could create a controlled lowered pH condition for a freely exchanging volume of seawater and with this in mind we began designing a new type of system where we could control both the addition of pH altering fluid and the current regime within a semi-enclosed system.

II. ROV BASED FOCE SYSTEM

A. FOCE reaction tube and flow generator

In order to simulate typical bottom currents it was necessary to match pump specifications to our control volume. Another determining factor was the dimensions of available pipe materials for constructing a reaction tube that would fit on the ROV. Based on these design criteria as well as time and budget limitations, a small ducted thruster (Deep Sea Systems Intl) was selected and installed within an 8 inch I.D. plastic duct hose, 4 meters in length (Fig. 2). Tank testing of these components demonstrated we could achieve the desired range of current velocities (2-5 cm/sec) and sufficient delay time (1-3 minutes) from the addition of CO_2 rich working fluid at the thruster to the end of the reaction tube.

B. FOCE Equilibrium Test Volume

The test volume was constructed with polycarbonate plastic and mounted to a rigid aluminum bar positioned in front of the ROV (Fig. 3). Sensors inside the test volume included four

Figure 2. FOCE system deployment using *ROV Ventana*.

commercially available sensors: three SeaBird 18 pH probes and one Falmouth 2" micro-CTD. Two pH probes and the CTD were positioned in the primary control volume (25cm x 25cm) while a third pH probe was located slightly downstream. If the hydration and hydroxylation of CO_2 in our test volume was complete, we would expect all three pH probes to read the same value so this third pH probe was a useful indicator of the extent of the reaction between the pH altering fluid and ambient seawater.

C. pH altering fluid reservoir

Carbon dioxide gas was actively bubbled through a 100 liter tank of 12^{o} C seawater for several hours. The resulting pH was measured to be 4.8 and 56 mM total CO_2 once the seawater had become equilibrated with the CO_2 gas. This low pH seawater was pumped into a 56-liter accumulator carried underneath the ROV (Fig 4). A small headspace of CO_2 gas was allowed to remain inside the accumulator so as to keep the seawater at a constant and lower pH. A hydraulic pump was used to dispense low pH seawater from the accumulator into a 20-liter collapsible bag. A small peristaltic pump could then be used to draw pH the altering fluid from this collapsible reservoir into our reaction tube and subsequently into the test volume. The use of a peristaltic pump ensured a constant and easily measured addition of low pH seawater. Depending upon the desired shift in pH the peristaltic pump speed could

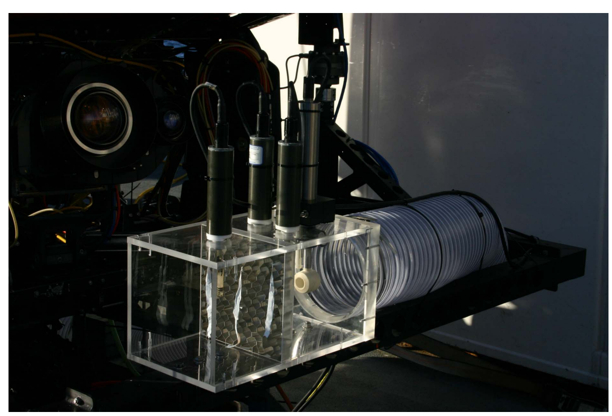

Figure 3. FOCE Equilibrium test volume containing pH probes and CTD.

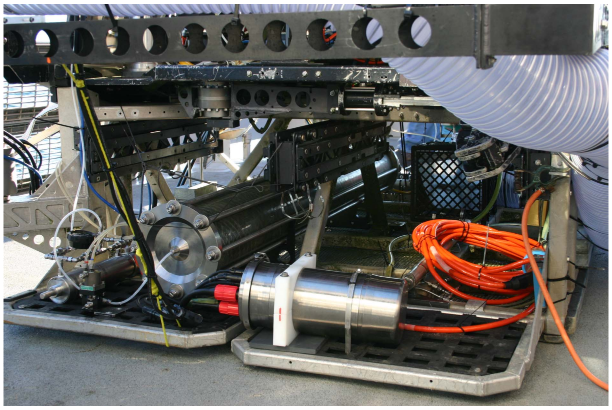

Figure 4. FOCE components on *ROV Ventana* toolsled.

be increased or decreased. Our predicted dilution of pH altering fluid into the control volume was 200:1 so our 56-liter supply was expected to last for several hours of experimental time once the ROV was on the seafloor.

D. Results

The ROV based FOCE system was deployed on October 24, 2007 in Monterey Bay, CA. All of the individual elements performed as expected. From the ship's ROV control room we could monitor and adjust the current speeds within the reaction tube, as well as the quantity of pH altering fluid added via the peristaltic pump. CTD and pH data was plotted in real time to a laptop computer also in the control room. Fig. 5 illustrates one example of in-situ data where pH was first reduced 0.9 pH units, returned to ambient pH, and then reduced again 0.6 pH units (red line). The CO_2/seawater reaction was not 100% complete however as the pH probe located downstream of the control volume area measured a slightly lower pH (blue line) due to the additional time for the CO_2 reactions to come to equilibrium.

III. CABLED FOCE SYSTEM DESIGN

FOCE was first envisioned as a system that could take advantage of cabled ocean observatories. The United States national ocean science community began looking at permanent ocean cables to bring high-speed communications and substantial power to the ocean floor in the 1990's [3, 4]. Since

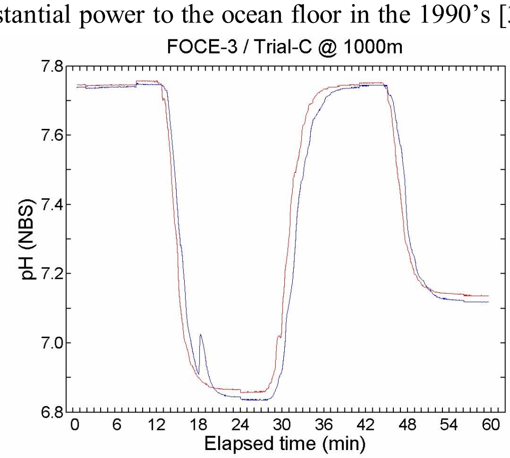

Figure 5. pH data from within the primary control volume (red line) and 20 cm downstream (blue line).

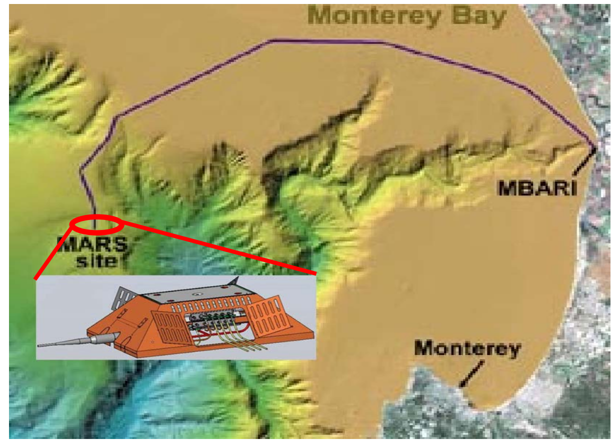

Figure 6. MARS Cabled Observatory, Monterey Bay, CA.

that time the push for more capable cabled observatory systems has continued [5]. MBARI proposed a cabled observatory test site for the development of instruments and techniques. MBARI was awarded a grant by the National Science Foundation (NSF) to build the Monterey Accelerated Research System (MARS) [6] shown in Figure 6.

The MARS cable delivers gigabit Ethernet and 10 kW of power to eight main ports which can be connected to by wet-mateable connectors. The systems main node will allow for extension nodes to be attached so that multiple experiments may use a main node port. This also allows for the experiments to be remotely located up to 5 km away with a single extension cable and expansion node. The experimental node is located at a site on a fairly smooth plateau at a depth of 843 meters. The temperature is very consistent at that depth as are the currents that have a direct correlation to the tidal signature. The operational numbers we have selected are 4° C and a current field varying from 25 cm/sec to -25 cm/sec.

As previously stated, the FOCE preliminary designs and tests to date have shown the system concept is viable. The only limiting factor is the supply of CO_2 required for a selected volume of ocean to be acidified for a science application. The driving factors for successful FOCE installations are the environmental factors such as temperature, currents, initial background pH, and so forth. The time delay required for a complete reaction is the main design driver for the mechanical portion of a FOCE system. Assuming a reaction is considered complete at any time past 2τ the system can be managed by creating delay loops based on the Zeebe and Wolf-Gladrow model (Fig. 7). The result is a system that is relatively simple with one dominant component that is the source of CO_2 to create the future world acidified ocean as predicted by the current models.

The FOCE system currently under construction to meet the functional criteria set by science is simple in construction. The system is being deployed in two phases for the purposes of engineering testing. The dominant material for the system is inexpensive plastic and aluminum. The first phase consists of testing the components previously untested in earlier FOCE prototypes. Those are mostly the interface elements that bring FOCE control to the desktop via the MARS cable. The controls as designed are based on a PC-104 computer with data storage, environmental, and communications boards. The

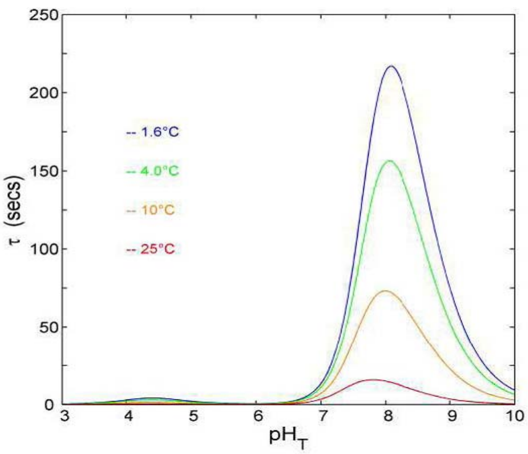

Figure 7. Curves from the Zeebe-Wolf Gladrow CO_2 kinetic model showing e-folding time at various temperatures as a function of pH.

Phase 1 system will demonstrate Internet control by science over the FOCE system and the ability to manage the currents and keep them within the specified regime. The system will be initially simplified by only completing one bi-directional section. The cruciform version (see Fig. 8) is intended to allow for currents from any direction and keep the most natural conditions for the species under study in the control volume. The control volume and the requirement to keep the space as natural as possible to the surrounding area is an important concern.

Years of experience diving MBARI ROVs in the Monterey Bay have illustrated that the detritus normal to the area falls at a very slow rate. After consulting with biologists at MBARI, a determination was made that creating a flume type design would be suitable to early modes of testing. This addressed a fundamental concern on how to constrain fauna that would otherwise escape the experimental system. The design also incorporates having an exposed underside allowing for the normal transit of bottom sediments and the associated detritus.

The driving equations for the control system are based on the kinetics of CO_2 chemistry in the environment. To accomplish this, the FOCE system must have knowledge of

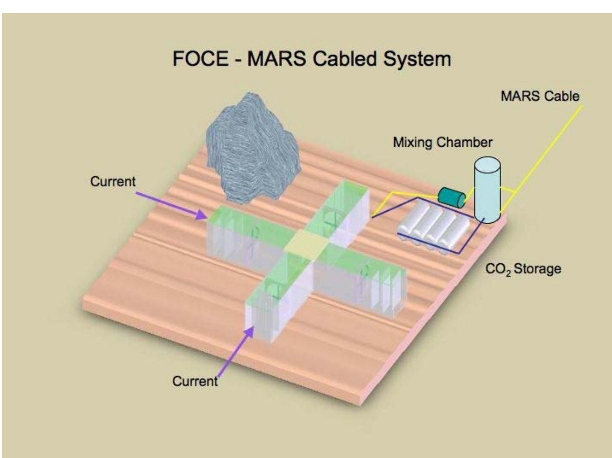

Figure 8. FOCE shown as deployed on the MARS system with a CO_2 delivery system.

Salinity, Temperature, Pressure, and local pH. A substitute of pCO_2 can be used to calculate local pH, which is the approach the FOCE system uses. Better sensor stability and reliability is readily available to provide the necessary data inputs. Currently, pH sensors suitable for the deep sea environment of the MARS cabled observatory are not proven to be stable or reliable for long term (months) deployment

The present FOCE design for the MARS cabled observatory includes specific features for science applications. The volume of the controlled area, approximately 1m x 1m x 0.5m in height, has a science port for power and communications to accommodate custom science instrumentation. The volume also includes a camera and lighting system to take still photographs on a scheduled basis as well as video based on science control. Phase 1 will not include pan and tilt for the camera but this will be included in Phase 2.

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