



High CO₂ and Ocean Acidification Research Using Cabled Observatories

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ABSTRACT

A primary design goal and challenge for a controlled sea-floor CO₂ enrichment experiment is to create a zone in which the perturbed fluid is at near equilibrium among the aqueous CO₂ system components. This is no easy task. CO₂ has no atmospheric chemistry, and so atmospheric CO₂ enrichment experiments are relatively easy to carry out although very large quantities of CO₂ (up to 1 thousand tons) are required. In sea water the slow reaction kinetics from any kind of CO₂ perturbation (acid or CO₂ addition) requires design and implementation of a long reaction path for transit between introduction point and experimental volume. The present FOCE design and control system achieves this by formally solving the CO₂ kinetic equations in real time, and providing feed-back from the pH or pCO₂ sensors to make adjustments in flow rate and quantity of CO₂ added. The design is parsimonious in CO₂ consumed, and can achieve about 80% of the desired equilibrium value under typical oceanic (T, velocity, and background pH) conditions. Power consumption is low (order of 200 watts) and a delta pH of up to 0.7 pH can be achieved using sea water enriched in CO₂ gas at 1 atmosphere as the perturbing fluid, mixed in at a typical ratio of ~ 1:200.

INTRODUCTION

In practice the reaction between CO₂ and H₂O is slow and is a complex function of temperature, pH, and TCO₂, 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 CO₂ equilibrium. Valid perturbation experiments must try to expose an experimental region to a stable lower pH condition, and avoid large and rapid pH variability.

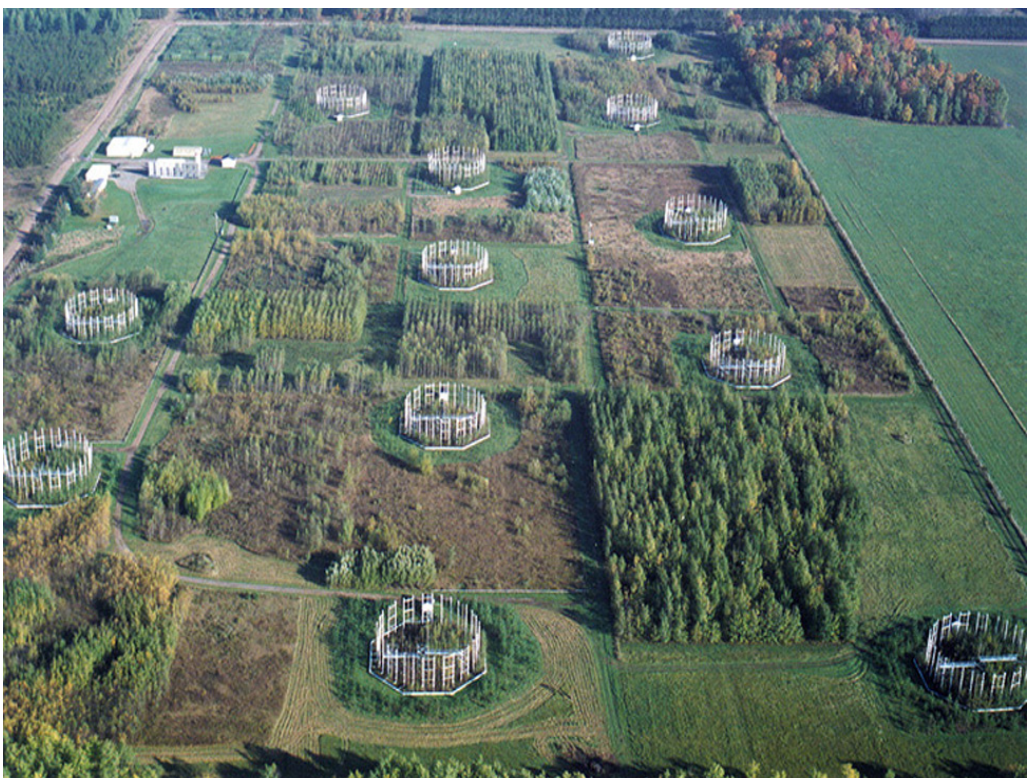
The most common sensor used for experimental control is the pH electrode, and this detects only H⁺ ion, not any of the dissolved CO₂ species. We first explored the reaction kinetics of a CO₂ perturbation in a series of closed loop pH cell experiments carried out at various depths under ROV control. These 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 CO₂ 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 CO₂ gas to create a solution of about pH 4.8 and 56 mM total CO₂. 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 CO₂-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 CO₂-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.



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. 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 CO₂ 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. Sensors inside the test volume included four 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 CO₂ 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°C seawater for several hours. The resulting pH was measured to be 4.8 and 56 mM total CO₂ once the seawater had become equilibrated with the CO₂ gas. This low pH seawater was pumped into a 56-liter accumulator carried underneath the ROV. A small headspace of CO₂ 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 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.

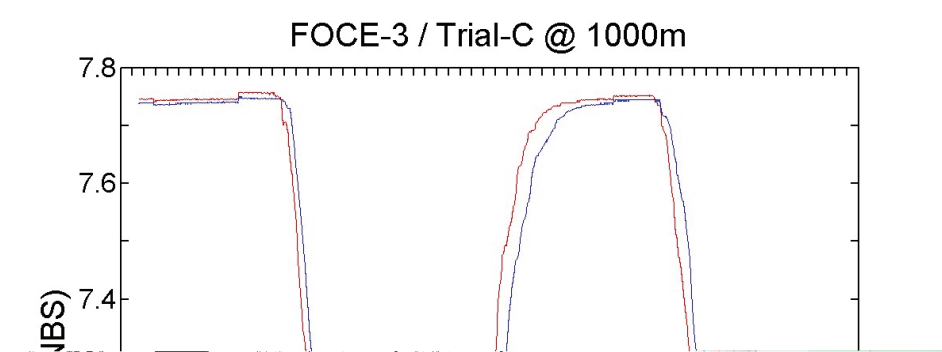
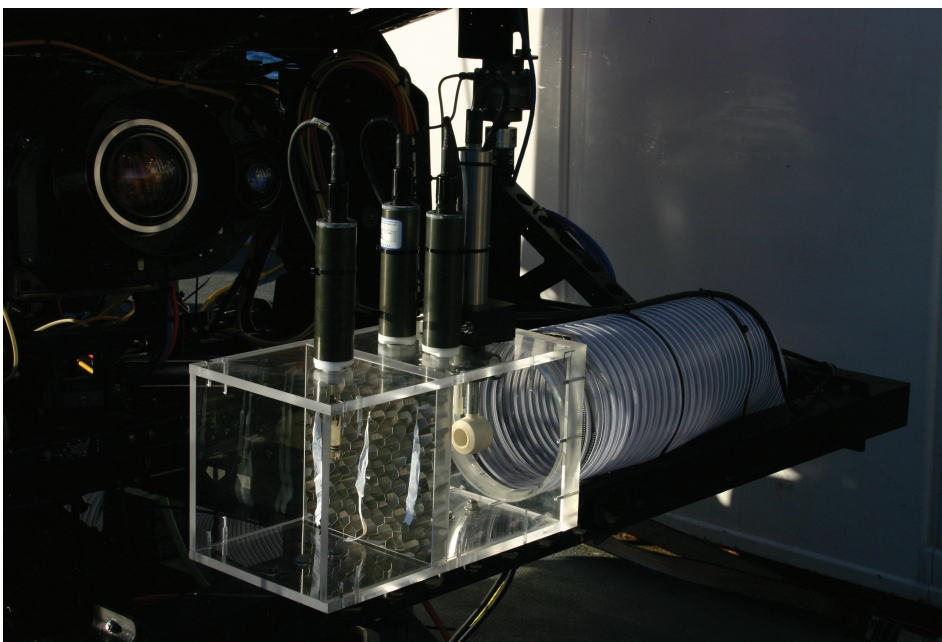
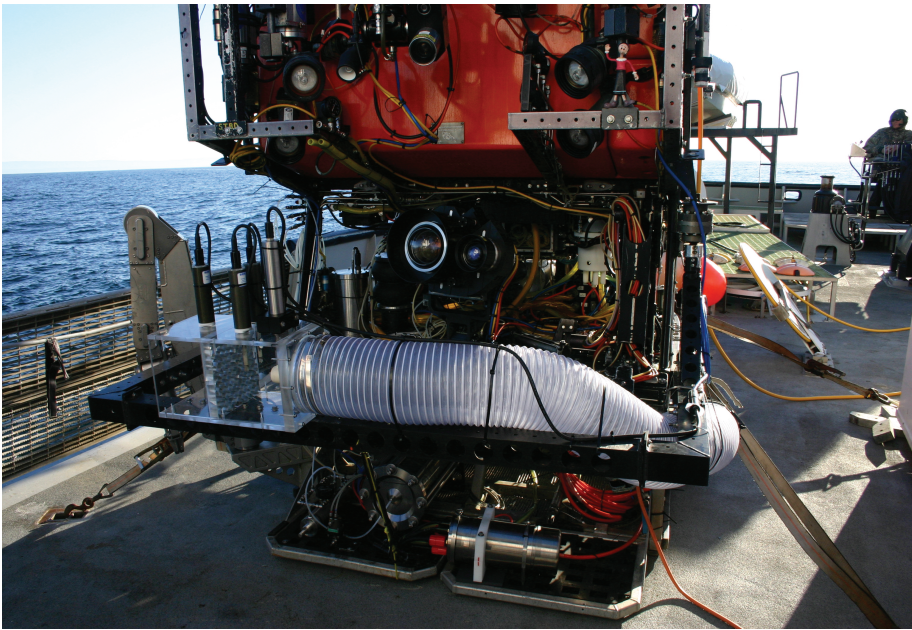
D. Results

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. The adjacent image 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 CO₂/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 CO₂ reactions to come to equilibrium.

CO₂ ENRICHMENT EXPERIMENTS ON LAND

Free Air CO₂ Enrichment (FACE) methodology has for decades been the standard for investigating the impacts of elevated atmospheric CO₂ levels on terrestrial ecosystems. It was widely believed that elevated atmospheric CO₂ levels would have a positive effect on growth of land plants. But concerns over the validity of enclosed greenhouse experiments arose.

In response a large international network of experiments was created, with CO₂ enrichment techniques being applied at many sites around the world through the creative endeavors of a large number of scientists. When the results were finally synthesized 20 years after the experiments were first proposed (Long et al., 2006) [7] a far lower CO₂ fertilization effect than first anticipated was found. Enclosed, and open, experiments can thus yield quite different results. Some 20 years later the ocean sciences face the same problem.



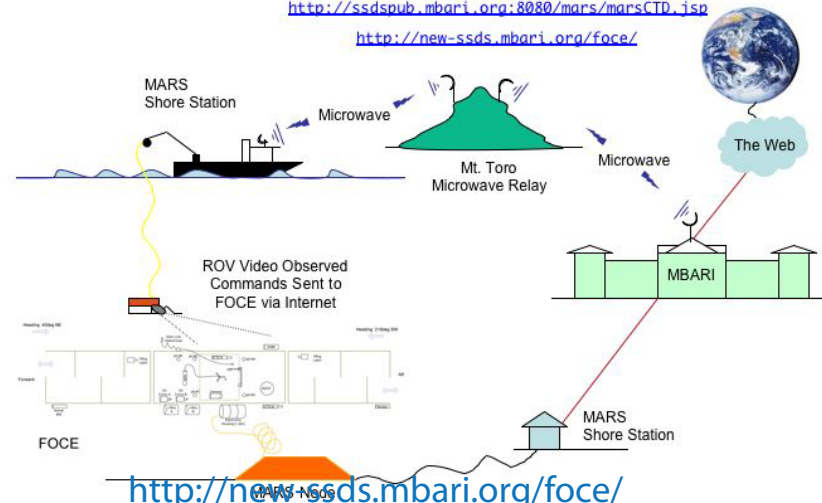
CABLED FOCE SYSTEM DESIGN

FOCE was created as a science experiment that can take advantage of the MARS cabled observatory. The efforts for cabled observatories started in the 1990's [3, 4]. Since 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]. MARS is now the national testbed for cabled observatories bringing high-speed communications and substantial power to the ocean floor.

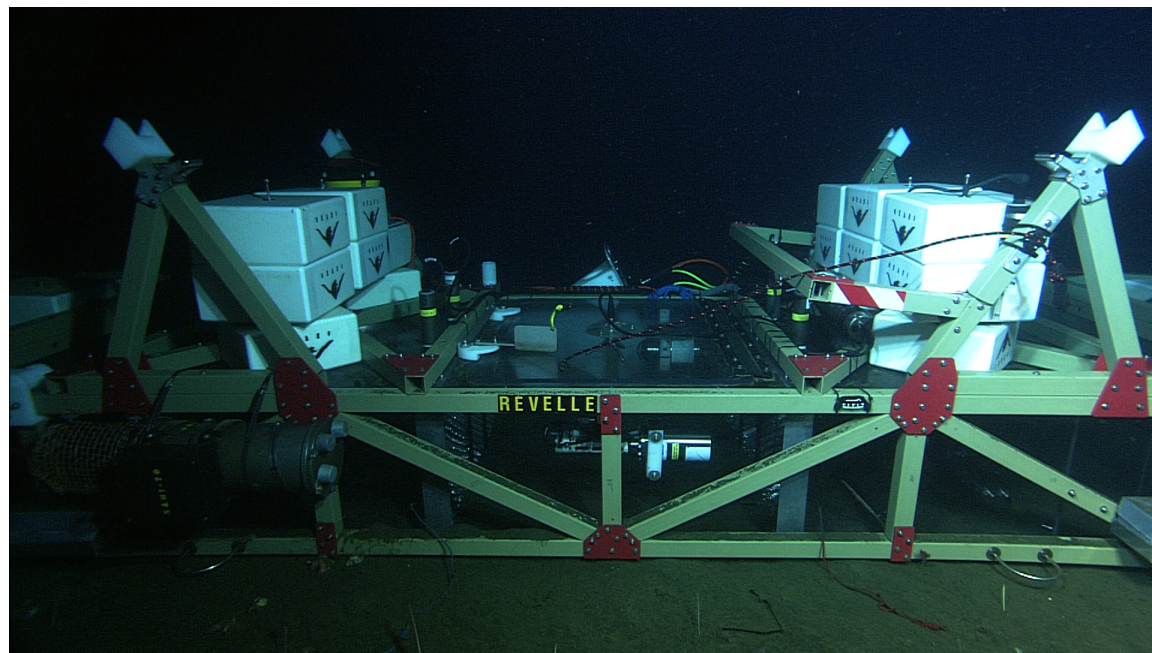
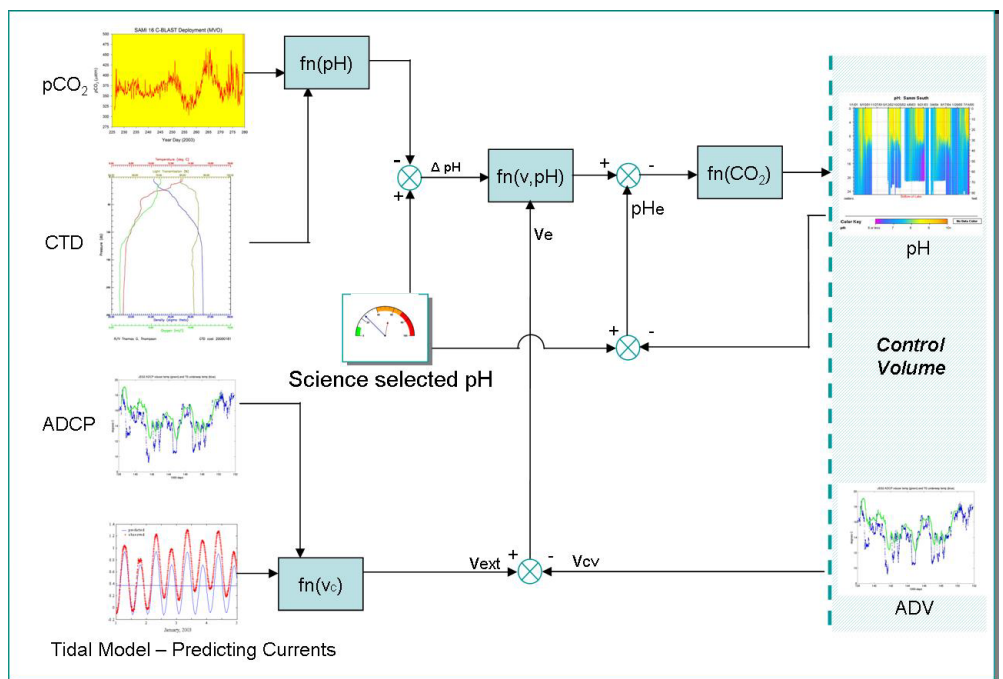
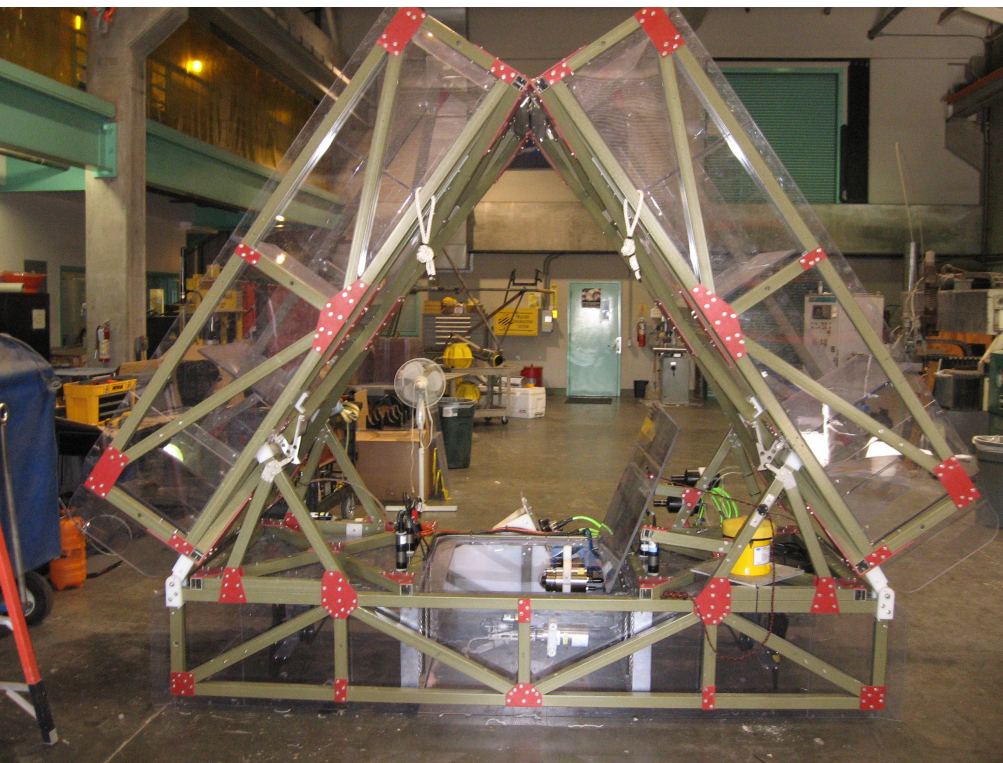
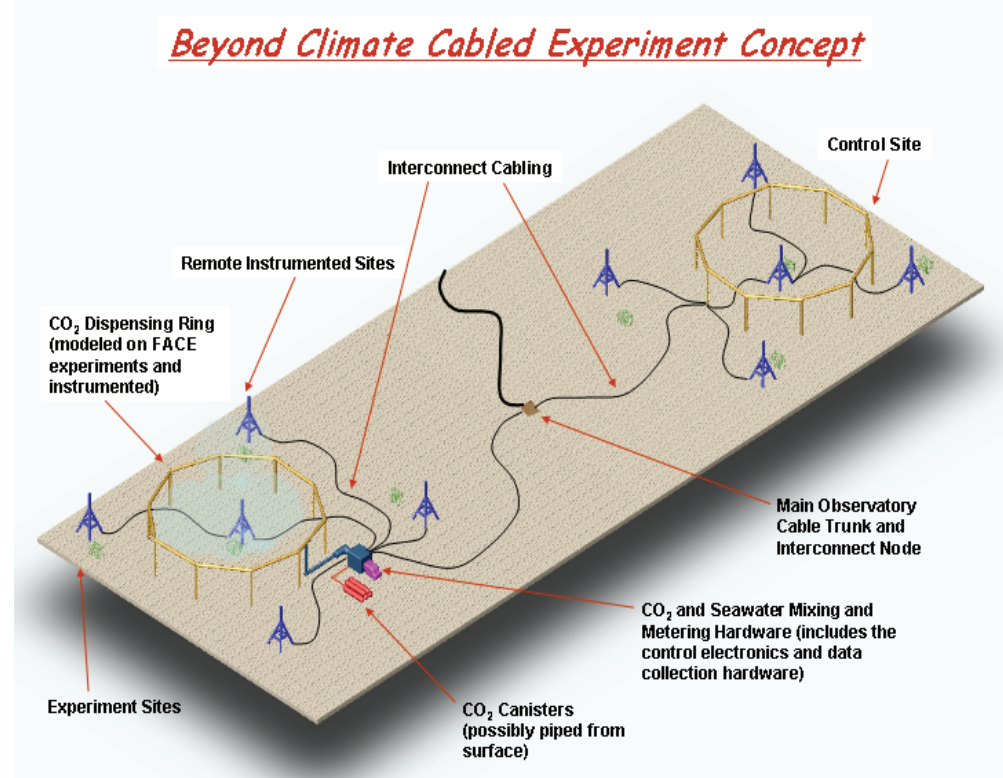
MARS currently delivers gigabit Ethernet and 10 kilo-Watts of power to eight main ports which can be connected to by wetmateable connectors. The systems main node allows for extension nodes to be attached so that multiple experiments may use a single main node port. This also allows for the experiments to be remotely located up to 5 km away with a single extension cable and expansion node. These expansion nodes can be linked to reach further distances. The MARS node is located in the Monterey Canyon on a fairly smooth plateau site at a depth of 843 meters. The temperature is very consistent at that depth as are the currents that have a predictable correlation to the tidal signature. The environmental numbers for FOCE are 4° C and a current field varying from 25 cm/sec to -25 cm/sec. As previously stated, the preliminary FOCE designs and tests to date have shown the system concept is viable. Although not difficult technically there is a challenge in supplying the CO₂ needed to acidify a given volume of ocean to a specific pH for a particular science experiment. Primary technical concerns for successful FOCE installations are the environmental factors such as temperature, currents, and initial background pH. Knowing these in real time sets the CO₂ injection volume and establishes the time delay for a complete reaction. The reaction time is strongly dependant on temperature and is the main driver for the mechanical portion of any FOCE system and preventing pH offset errors.

After consulting with biologists at MBARI, a determination was made that creating a flume type design would be suitable for early deep sea 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. For proper function FOCE systems must have knowledge of Salinity, Temperature, Pressure, and local pH. To calculate background pH pCO₂ can be used. Seabird pH sensors are used for the internal dynmaic reaction readings. However, they have 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 1 m x 1 m x 0.5m in height, has a science port for power and communications to accommodate custom science instrumentation. The volume also includes a pan & tilt camera with lighting system to take still photographs on a scheduled basis as well as video based on science control.

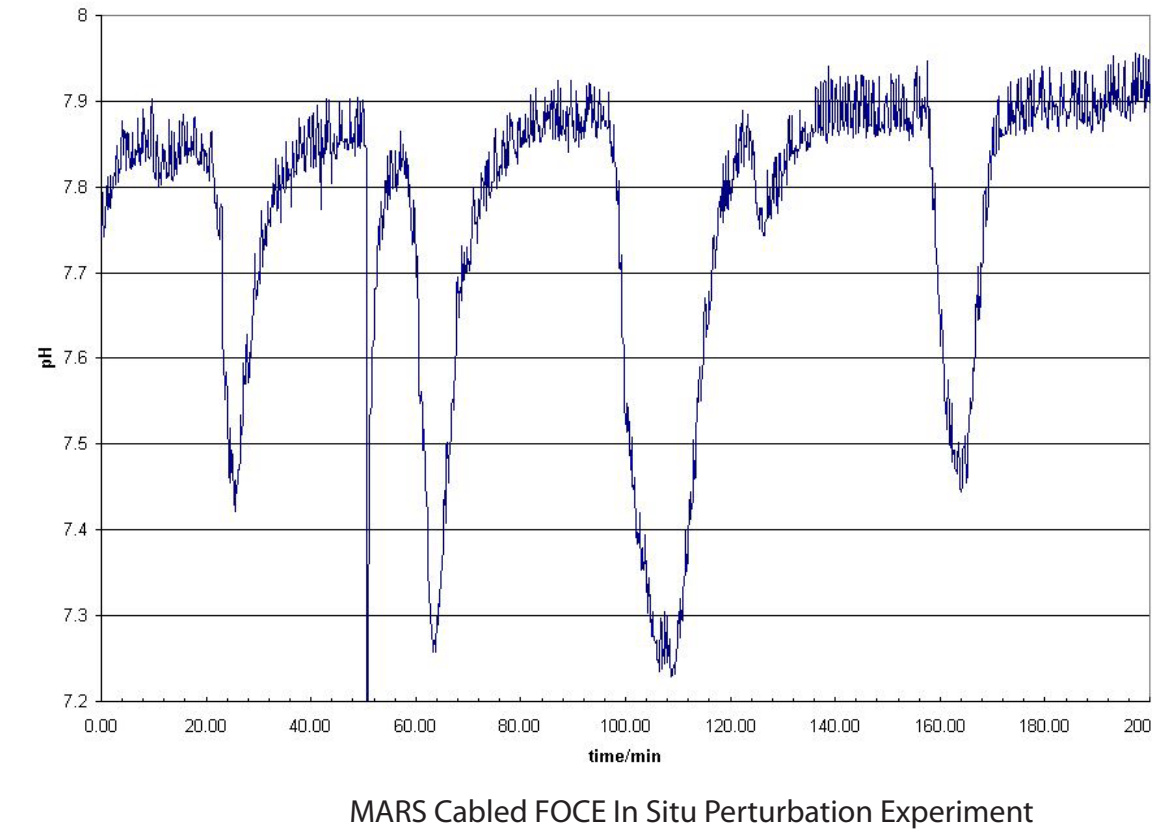
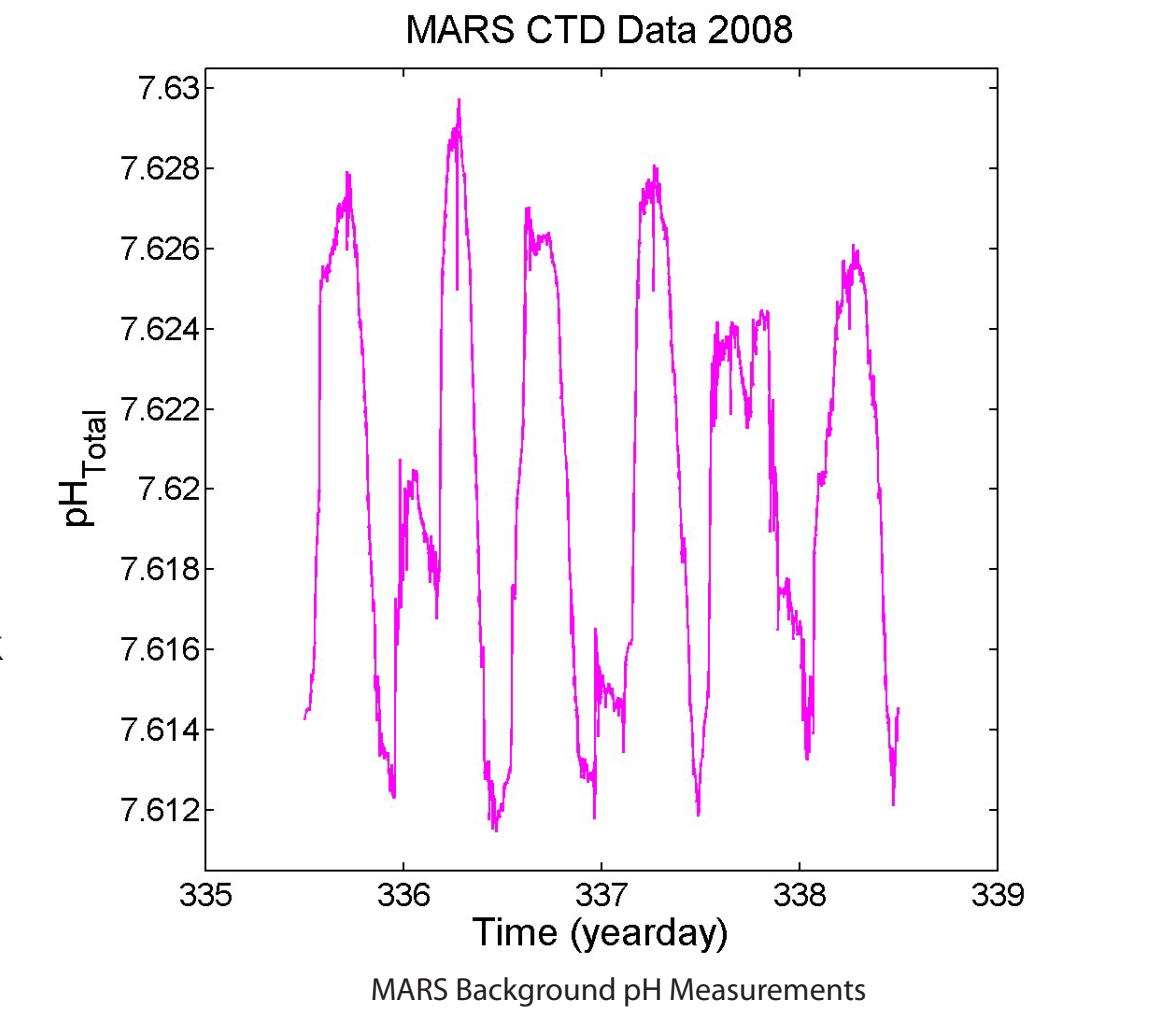
The deep sea FOCE system (shown right) is currently installed on MARS for engineering tests to evaluate the core functionality. This first phase consists of testing the core components previously untested in earlier FOCE prototypes as well as the plug and work supporting technologies. The installation took place on December 8th of 2008. Once the FOCE system was plugged into MARS, it took about 30 seconds from power up for FOCE to boot up. Data was immediately captured and stored by MARS without prompting. Web based data plots were retrieved at sea in real time with the data interface provided by the Shore Side Data System via the microwave link to the ship. Prior to leaving the installation FOCE velocity commands were given and verified by the data stream. Below is a block diagram of the end to end communications that took place, prior to leaving the installation.



The second phase will have the addition of the long endurance CO₂ injection sub-system. The second tests are currently scheduled for early spring of 2009.



FOCE Installed on the MARS Cabled Observatory



CORAL REEFS AND OCEAN ACIDIFICATION

While much of the recent focus has been on reef-building corals (Kleypas and Langdon 2006) [8], there is growing evidence that ocean acidification will have significant impacts on a wide range of reef-associated organisms and biological processes. Our understanding of these impacts and underlying mechanisms, however, is minimal and must be rapidly improved if we are to comprehend the full gamut of vulnerabilities arising from ocean acidification (Raven et al. 2005) [9]. Proposed Climate Change Observatories will rapidly improve our understanding of climate change impacts on coral reefs by providing fine scale data on the physical and chemical changes to the seawater flushing across a coral reef and the first data on the response of an intact coral reef flat community to future CO₂ levels.

The in-situ acidification experiment will provide data previously unobtainable from earlier coral reef acidification experimental studies. Prior studies relied mostly on laboratory based aquaria experiments with coral fragments. These had numerous limitations including modified physical parameters (including light, water flow, and water temperatures), biological parameters (associated with having broken fragments of corals without their associated biota) and chemical parameters (by excluding the natural benthos that could serve as buffers to the changing pH).

Experiments based on a technology to inject CO₂ in to the center of a ring structure that has been used successfully on land for over 15 years (Ainsworth 2005) [9]. This technology has been developed by MBARI for the marine environment but this will be the first application on a coral reef. Hopefully a successful proposal can be the start of a global network of Coral FOCE experiments.

BROADER IMPACTS

The broader impacts of this work are many. There does not now exist a way to carry out controlled perturbation experiments in the ocean to investigate the impacts of elevated CO₂ -lower pH levels. The successful development of this technology could provide a working method that could be adopted and modified by research groups around the world. Our survey of the field has shown great interest in this. All system specifications will be open, as will the control software code. There is great policy interest at high levels of government on the impacts of high CO₂ levels, in the health of the ocean, and in its living resources.

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