

Creating controlled CO₂ perturbation experiments on the seafloor – Development of FOCE techniques

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We report recent progress on the design and testing of systems for carrying out controlled CO₂ perturbation experiments on the sea floor with the goal of simulating the conditions of our future high CO₂ world. Controlled CO₂ enrichment (FACE) experiments have long been carried out on land to investigate the effects of elevated atmospheric CO₂ levels on vegetation, but only limited work on CO₂ 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 pH of 0.3 to 0.5 by addition of CO₂, 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, CO₂ has complex chemistry in seawater with significantly slow reaction kinetics. One must design systems to take this into account. The net result of adding a small quantity of CO₂ to sea water is to reduce the concentration of dissolved carbonate ion, and increase bicarbonate ion through the following reaction:



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 the simple dissolved CO₂ molecule. 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 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 1,000 m depth. 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 L piston accumulator, and dispensed as needed into a flexible polyethylene bag for subsequent addition into the experimental unit.

The design consisted of a 4 m 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.