Instruments and Methods

Design, construction, and operation of an actively controlled deep-sea CO$_2$ enrichment experiment using a cabled observatory system

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A R T I C L E   I N F O

A B S T R A C T

We describe the design, testing, and performance of an actively controlled deep-sea Free Ocean CO$_2$ Enrichment (dp-FOCE) system for the execution of seafloor experiments relating to the impacts of ocean acidification on natural ecosystems. We used the 880 m deep MARS (Monterey Accelerated Research System) cable site offshore Monterey Bay, California for this work, but the Free Ocean CO$_2$ Enrichment (FOCE) system concept is designed to be scalable and can be modified to be used in a wide variety of ocean depths and locations. The main frame is based on a flume design with active thruster control of flow and a central experimental chamber. The unit was allowed to free fall to the seafloor and connected to the cable node by remotely operated vehicle (ROV) manipulation. For operation at depth we designed a liquid CO$_2$ containment reservoir which provided the CO$_2$ enriched working fluid as ambient seawater was drawn through the reservoir beneath the more buoyant liquid CO$_2$. Our design allowed for the significant lag time associated with the hydration of the dissolved CO$_2$ molecule, resulting in an e-folding time, τ, of 97 s between fluid injection and pH sensing at the mean local $T = 4.31 \pm 0.14$ °C and pH$_T$ of 7.625 $\pm$ 0.011. The system maintained a pH offset of $\sim$0.4 pH units compared to the surrounding ocean for a period of $\sim$1 month. The unit allows for the emplacement of deep-sea animals for testing. We describe the components and software used for system operation and show examples of each. The demonstrated ability for active control of experimental systems opens new possibilities for deep-sea biogeochemical perturbation experiments of several kinds and our developments in open source control systems software and hardware described here are applicable to this end.

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1. Introduction

With the recent introduction of cabled observatory systems (Favali and Beranzoli, 2006; Massion and Raybould, 2006; Favali et al., 2010) new opportunities for deep-sea experimental science have arisen. While many of the instruments that have been deployed on such cables can report in real-time through their power and optical fiber connectivity they are still in a sense passive instruments that simply record the events of the natural world around them.

We describe here the creation of an actively controlled deep-sea experimental system for investigation of the impacts of elevated oceanic CO$_2$ levels on seafloor marine ecosystems from concept through design, testing, and construction into full

operation. The system may also be adapted to experiments controlling dissolved O$_2$ levels or for a combination of CO$_2$ and O$_2$ perturbation experiments. Although the system described here was developed for deep-sea operation, the intent has been to understand the fundamental physical and chemical principles involved in order to produce a fully scalable system with sufficient design flexibility so that other deep and/or shallow water systems of varying dimensions can be adapted from it. This technology transfer process is already occurring at several other Free Ocean CO$_2$ Enrichment (FOCE) sites (Kline et al., 2012; Gattuso et al., 2014).

The impetus for creation of a pH controlled experimental system may be traced to concerns that arose when small-scale direct deep-ocean CO$_2$ disposal experiments were carried out at a depth of 3600 m (Brewer et al., 1999). These efforts were driven by the recommendations of a US President's Council of Advisors on Science and Technology report (PCAST (President's Council of Advisors on Science and Technology), 1997) that, following an idea first

suggested by Marchetti (1977), advocated direct disposal of captured fossil fuel CO_2 in the deep ocean where it was presumed a stable solid hydrate would form. The images from that deep-sea experiment of a fish swimming by a beaker of overflowing liquid CO_2, driven by formation of solid CO_2 hydrate, stimulated long-latent awareness of both the true scale of future fossil fuel CO_2 emissions and the difficulty of dealing with this (Cicerone et al., 2004; Shirayama and Kogure, 2004; IPCC, 2005). Until that time the beneficial role of large scale ocean absorption of fossil fuel CO_2 from the atmosphere was the dominant focus of scientists, although in retrospect the warning signs of the forced changes in ocean chemistry were present for many decades (Brewer, 2013). Simultaneously with the interest in direct deep-ocean CO_2 disposal, large scale under-sea geologic sequestration of CO_2 produced from off-shore oil and gas fields began and questions over the impact of any future seafloor CO_2 leakage arose (Widdicombe et al., 2013).

Early experiments on biological impacts of artificially elevated CO_2 levels in the deep sea (3600 m) were reported by Tamburri et al. (2000) and by Barry et al. (2004, 2005). These were carried out with single pools of liquid CO_2 as the CO_2 source. The physical properties of liquid CO_2 are such that at depths below about 2600–2800 m (depending upon the in situ temperature) it is denser than sea water and thus gravitationally stable on the seafloor (Brewer et al., 1999). This allows experimental emplacement of an open pool of liquid CO_2 that creates a dense plume of low pH water as the CO_2 dissolves into the surrounding seawater. When these first experiments were conducted to assess the impact of low pH/high CO_2 seawater on local marine life it was quickly realized that the effect of the local tidal ellipse was to create a highly variable diurnal ΔpH signal which greatly exceeded the natural background variations.

These experiments, while accurately depicting the locally varying small-scale pH field around a liquid CO_2 disposal event, did not provide a useful way of assessing long-term marine life impacts of a future high CO_2 ocean although valuable short term impact studies emerged (Thistle et al., 2006, 2007); animals at a specific site were exposed to a low pH/high CO_2 plume for only a short time twice a day. To be useful for long-term assessment of biological and organismal impacts of ocean acidification some greater degree of control over CO_2 enrichment and flow rate within a specified volume is required so that a reasonably constant pH offset above the varying natural background can be maintained.

We realized that lessons could be learned from the global series of FACE (Free Air CO_2 Enrichment) terrestrial ecosystem experiments (DeLucia et al., 1999; Shaw et al., 2002). That effort demonstrated that experiments within greenhouses showing strong stimulation of plant growth from elevated atmospheric CO_2 levels might not apply to the real, more complex, open world of climate change. The net result from a very large number of these FACE field experiments was that natural land ecosystems would benefit little, if at all, from elevated CO_2 levels (Long et al., 2006).

Similarly, aquaria pH perturbation experiments might not adequately represent impacts on complex ecosystems and careful in situ studies may show problems, or resilience and abilities to compensate in some species. We will not know unless competent experiments at a wide variety of sites can be carried out and we can advance beyond single species aquarium studies; here we describe progress in creating such field experimental systems.

2. Initial studies

2.1. First attempts at a CO_2 enrichment control system

Three principles guided the design and operation of the FOCE experimental system. (1) The system needs to be "open to the ocean" in such a way that natural variations in S, T, P, O_2, TAlk and food supply are not altered. Unlike experiments in aquaria where these parameters are often held constant, FOCE experiments should reflect natural variations and diurnal to seasonal cycles as much as possible. (2) The system is intended to be a total CO_2 enrichment experiment not a pH experiment. TCO_2 levels are increased without changing the alkalinity in order to achieve pCO_2 levels predicted for the next century through the addition of dissolved CO_2, not by the addition of bicarbonate or strong mineral acids. (3) The resulting change in pH is used to monitor the change in TCO_2 and pCO_2 in order to provide real-time feedback and control of the CO_2 addition.
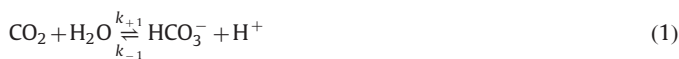
On land the tactic has been to encircle an area of vegetation with a ring of controlled CO_2 gas emitters programmed to release only from the upwind sector of the ring. It is clear that very different experimental constraints apply in the ocean. The physical forces on the apparatus are larger, and the experimental set-up is more challenging whether by scuba divers or by remotely operated vehicles (ROVs). Most importantly, CO_2 in sea water has a complex chemistry with significant reaction rate kinetics (Zeebe and Wolf-Gladrow, 2001) that greatly impacts the ability to sense and thus control a plume of CO_2 enriched sea water (Brewer et al., 2005). In our Supporting Information, we describe the early experiment development which began with a simple ring structure system test. This quickly led to the need for providing a delay time between addition of the CO_2 rich working fluid and the observation chamber to allow time for the hydration of the aqueous CO_2 molecule to proceed and thus provide the desired pH perturbation.

2.2. Experimentally defining the chemical reaction rates and design implications

The essential chemical reaction rates for the hydration of CO_2 in sea water have been carefully observed in the laboratory (Johnson, 1982; Soli and Byrne, 2002). This information was gathered and incorporated into a rigorous theoretical treatment by Zeebe et al. (1999) and Zeebe and Wolf-Gladrow (2001). The end result is a series of equations where the relaxation time, τ, is dependent upon total CO_2 concentration, temperature, pressure, and the final pH of the system.

We have conducted the essential field measurements of these basic reaction rate equations developed from laboratory data in the deep waters of Monterey Bay. We used a closed cell pH perturbation technique first reported by Nakayama et al. (2005) in which we used a ROV (Fig. 1a) to carry and control a simple titration cell (Fig. 1b) to depth and followed the time course of the pH curve resulting from injection of various volumes of CO_2 saturated seawater (Fig. 1c and d). The pH data within the cell as a function of time obtained in situ was first converted into the concentration of OH^- and the best fit to the exponential decay curve was then found to determine the experimentally measured τ. These experiments are fairly quick to execute and within a single ROV dive we were able to make measurements over a span of temperature, pressure, pH and δCO_2 conditions.

The Zeebe and Wolf-Gladrow (2001) CO_2 kinetic model is based upon the interaction of the two competing reactions of CO_2 with water as a function of pH:

$$CO_2 + H_2O \underset{k_{-1}}{\overset{k_{+1}}{\rightleftharpoons}} HCO_3^- + H^+ \tag{1}$$

$$CO_2 + OH^- \underset{k_{-4}}{\overset{k_{+4}}{\rightleftharpoons}} HCO_3^- \tag{2}$$

the dissociation of bicarbonate ion and the dissociation of water:

$$HCO_3^- \rightleftharpoons CO_3^{2-} + H^+ \tag{3}$$