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ABSTRACT

Direct ocean injection of CO_2 is one of several approaches under consideration to sequester carbon dioxide in order to stabilize atmospheric CO_2 near 550 ppm (2X preindustrial CO_2 levels). Without significant efforts to stabilize greenhouse gas emissions, the Earth is expected to experience extreme climate warming consequences associated with the projected high (~3-4X pre-industrial) atmospheric CO_2 levels in the next 100 to 200 years. Research funded by DOE-Office of Fossil Energy under this award is based on the development of novel experimental methods by MBARI to deploy small quantities (5 - 45 l) of liquid CO_2 in the deep-sea for the purposes of investigating the fundamental science underlying the concepts of ocean CO_2 sequestration. This project is linked closely with studies funded by the Office of Science and the Monterey Bay Aquarium Research Institute (MBARI).

The objectives of studies in marine chemistry funded by the Office of Fossil Energy and MBARI are to: **1.** Determine the long term fate of CO_2 hydrate in the deep-sea, **2.I**investigate the geochemical changes in marine sediments and pore waters associated with CO_2 disposal, and **3.** Investigate the transfer of CO_2 from the hydrate phase to the oceanic water column as a boundary condition for ocean modeling of the fate of the released material. These activities extend the results of recent studies using the deep-sea CO_2 deployment system, which characterized several features of liquid CO_2 released into the sea, including hydrate formation and factors influencing dissolution rates of CO_2. Results from this project are relevant in determining the efficacy of carbon sequestration and the degree of perturbation of seawater chemistry.

Biological studies, funded jointly by the Office of Science, Office of Fossil Energy, and MBARI, focus on the environmental consequences of CO_2 release in the deep-sea. The specific objectives include: 1. Determination of the survival rates of typical deep-sea species exposed to changes in seawater chemistry (i.e. pH reduction, CO_2 elevation) expected with ocean carbon sequestration, 2. Characterization of sublethal effects of CO_2 exposure, such as changes in rates of respiration, growth, and reproduction, and 3. Comparative investigation of physiological effects of CO_2 exposure on species typical of deep-sea (i.e. >1000 m) and shallow (i.e. 0 -200 m) marine environments.

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Experiments & Results of Ocean Chemical Studies to Date

Large Volume CO_2 Delivery System

Our early work on deep-sea CO_2 delivery (Brewer et al., 1999) was based upon a 7 liter volume steel accumulator, used to deliver liquid CO_2 to the sea floor at depths >3000m. We have had designed and constructed a new 45 liter accumulator, with a body of carbon fiber composite and steel end caps (see diagram). The larger size was desired so as to observe macroscopic effects of sediment coverage, and to achieve longer life times of deposited CO_2 pools for valid biological observations.

Line drawing of the 45 L accumulator body. The body is of carbon fiber composite. Dimensions are 79.5" long, 11" diameter.

Steel tie rods run the length of the body to accommodate pressures of 1500 psi. The piston is actuated by pumping sea water into the open end of the system during the dive to compensate for gas phase condensation to liquid, and also for the high compressibility of CO_2 relative to sea water.

This unit has now been used several times at depths of 3600m to deposit approximately 35 liters of liquid CO_2 per dive. This unit represents about the maximum size and weight possible for deployment with MBARI's ROV Tiburon.

Time Lapse Camera Study

We had earlier acquired a time lapse camera (Sony Hi-8) and pressure housing for deep-sea studies. Funds provided here enabled new battery pack purchases, and field deployment. This camera was deployed adjacent to a corral (20 inch diameter) filled with liquid CO2 on the sea floor at 3600m depth. The camera was set to illuminate and record 30 seconds of video of the corral every 30 minutes for 14 days.

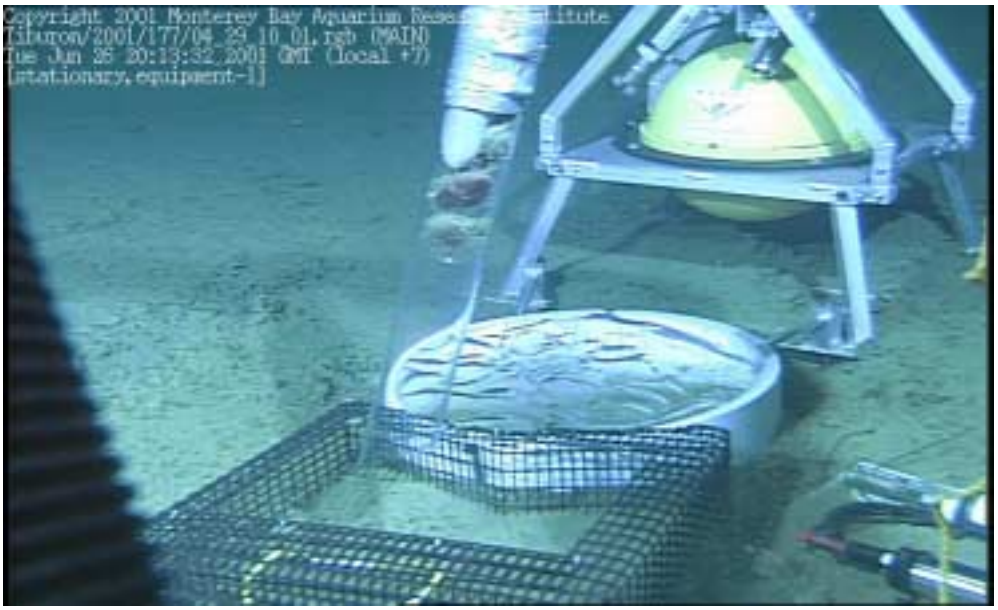


Image of MBARI time lapse camera at 3600m depth positioned in front of CO_2 corral and cages that are to be populated with sea urchins and sea cucumbers.

A full data set was recovered and is being processed. Early inspection however shows simple slow dissolution, with no obvious animal visits or other behaviors. Full dissolution was achieved very close to the end of the 14 day observation period.

Evidence for Chaotic or Stochastic Behavior

We now have evidence of multiple outcomes of apparently identical experiments, indicating the potential for stochastic or chaotic behavior. This is possible in 3+ component (CO_2, water, hydrate, salt etc.) interacting systems.

Examples include:

1) In a recent repeat of the "overflowing beaker" experiment (Brewer et al., 1999) we found no evidence of creation of self sustaining convection from hydrate formation. In pressure vessel experiments carried out in Japan (I. Aya, pers. comm.) it was also reported that this was possible, and attributed to small changes in initial conditions – specifically the availability of water channels separating lobes of liquid CO_2 which provided routes for sinking of dense boundary layer fluids.
2) In adjacent sea floor corral studies we have observed both passive dissolution from the liquid state (covered with a ~ 1μm thick hydrate skin) over a 14 day period (see paragraph above). And apparent rapid (within 24 hours) sediment penetration of CO_2 rich fluids, followed by nucleation of hydrate, and creation of a solid hydrate mass which projects as a "frost heave" through the sediment surface.

Image of 20" diameter corral of liquid CO_2 on the sea floor at 3600m depth. The corral was filled about 24 hours earlier. Apparently diffusion of CO_2 through the hydrate film has resulted in flow of dense CO_2 saturated fluid into the sediment. A nucleation event has occurred, and massive hydrate formation has followed. This has thrust upwards creating a "frost heave" reminiscent of methane hydrate observations. Both CH_4 and CO_2 form a Structure I hydrate.

Taken together these results indicate that multiple outcomes are possible in the short term, and that caution should be exercised in interpreting results, or theorizing on processes based on few data.

Direct Measurement of the Dissolution Rate at 3600m depth

No matter the pathway taken (see above) the longer term fate of CO_2 deposited in the ocean is to dissolve in sea water. This is true whether the material is present as a solid hydrate, or simply as a liquid protected by a hydrate film. We have measured the dissolution rates of both the solid hydrate, and of liquid CO_2 covered with a hydrate film.

For the latter case we were able to take advantage of an unusual property of liquid CO_2 films in contact with sea water *under-saturated* with CO_2. In this case penetration of the film by a solid object results not in a simple elastic deformation, but an active rebuilding of the hydrate film so that large extensions are possible (I. Aya et al., 2001).

In a unique experiment with MBARI summer intern Rachel Dunk (Southampton Oceanography Center, England) we slowly inserted a pH electrode, surrounded by a protective metal grid, up to 4 cm into a mass of CO_2 on the sea floor at 3600m depth. This created a pocket of sea water within the CO_2.

Initial pH values were very close to background sea water, but slowly dropped over a 20 minute period as CO_2 diffusion through the membrane occurred. By assuming constant alkalinity we were able to use the pH data to compute a CO_2 transfer rate of 1.7 μmol/cm^2/sec.

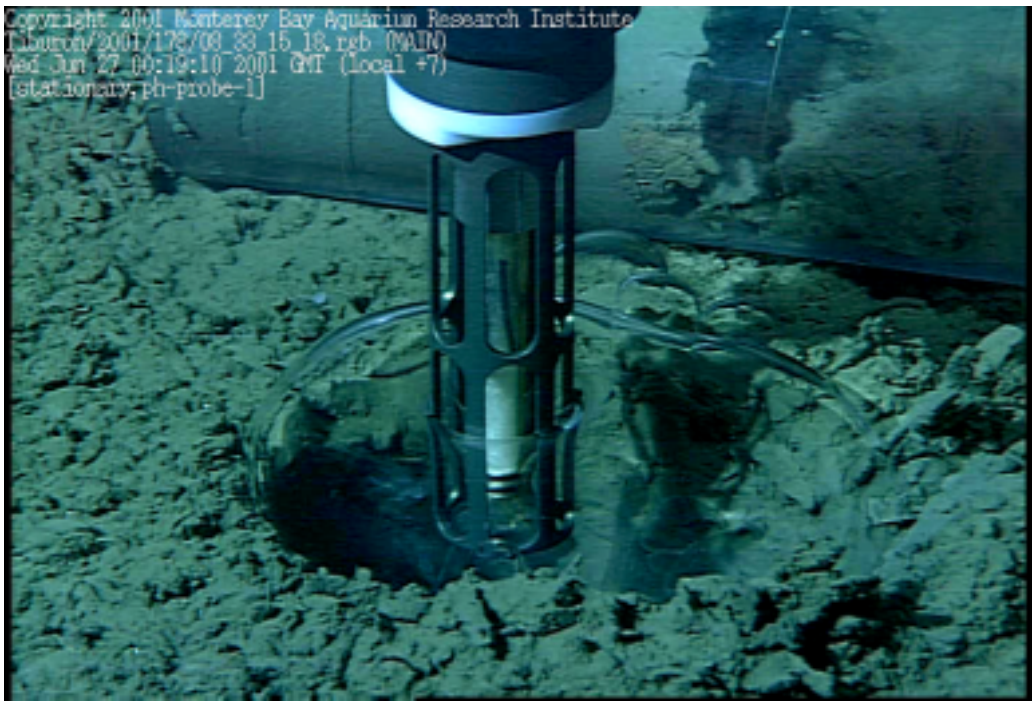
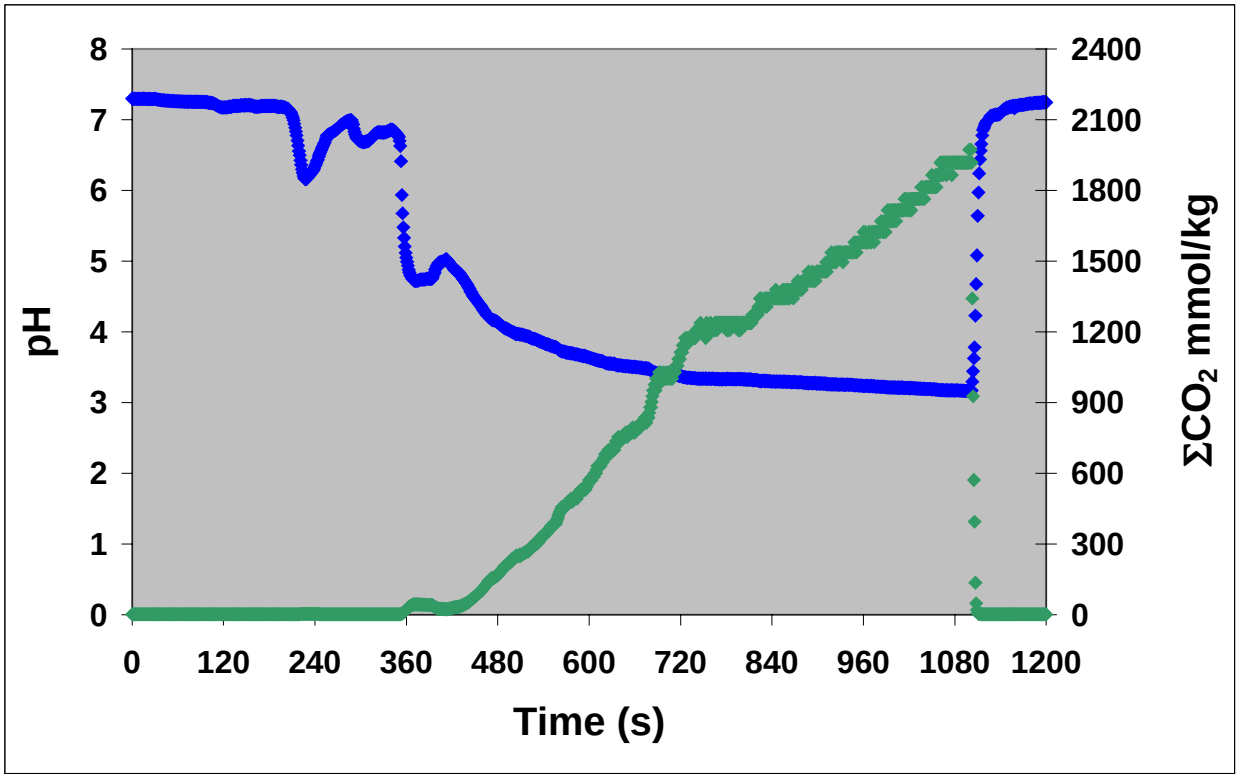


Image of MBARI pH probe inserted ~ 4cm into a liquid CO_2 mass. The surface has not deformed, but has rebuilt the hydrate film by crack filling. Diffusion of CO_2 through the film into the water pocket occurs.

Data on pH, and computed CO_2, obtained from the experiment above.



Results of Biological Studies to Date

DOE / MBARI Carbon Dioxide Sequestration Experts Workshop

A workshop including experts in direct ocean carbon dioxide sequestration from several disciplines was hosted by Peter Brewer at MBARI. Jim Barry and Brad Seibel (a postdoctoral fellow funded by grant no. DE-FG03-01DF63065) participated in the workshop, presenting an overview of biological studies in this project and contributed to a draft workshop report on the biological consequences of CO_2 sequestration.

Deep-sea CO_2 Release Experiment I

Objectives

Initial field experiments to evaluate the effects of deep-sea CO_2 release on seafloor biological communities were designed and performed by Brewer and Barry. The biological objectives of this field experiment were to evaluate the response (survival and physiological changes) of a variety of benthic organisms to CO_2 exposure and changes in seawater chemistry associated with CO_2 sequestration.

Approach

Changes in the survival and physiological condition of benthic organisms were compared between groups exposed to CO_2 and control groups. The field experiment, made possible by the deep-sea CO_2 deployment system and the capabilities of MBARI's ROV Tiburon, consisted of triplicate pools of liquid CO_2 (~15 l each) were released into 0.5 m diameter x 15 cm high corrals placed on the sea floor at 3600 m, approximately 85 nautical miles west of Moss Landing, CA (Figure 1). Triplicate "control" corrals were placed nearby on the seafloor, but were not filled with CO_2 (Figure 2). Dissolution of CO_2 into ambient currents resulted in a CO_2-rich plume trailing down-current from the corrals containing CO_2. Perturbations of normal seawater chemistry were determined by changes in pH measured near the CO_2 pools. Local currents were measured using an acoustic Doppler current meter, moored near the seafloor at the study site.

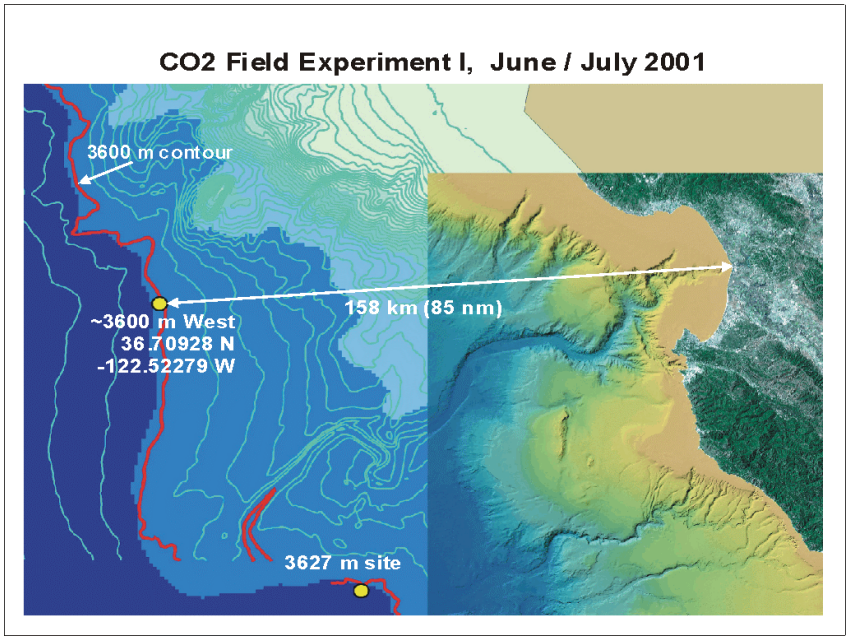


Figure 1. Location map of CO2 field experiment I.

In addition to observations of hydrate formation and dissolution, studies of the responses of several faunal groups to CO_2 exposure are ongoing. First, the survival and physiological responses to CO_2 exposure of two species of benthic megafauna two echinoderm species, a sea urchin (echinoid sp. 1), and a sea cucumber (Holothurian sp. 1), were evaluated. Both species are common sea floor megafauna at the study site. In the experiment, several individuals of each species were collected from the study area and placed in mesh cages directly adjacent to both the CO_2 corrals and the control corrals. Second, changes in the abundance and metabolic condition of infaunal organisms (worms, crustaceans, etc.) and meiofauna (protistan fauna) were compared between CO_2 and control treatments, based on sediment cores collected before and after the experiment in the vicinity of CO_2 and control corrals. Third, differences in the abundance of microbial organisms were compared among treatments.

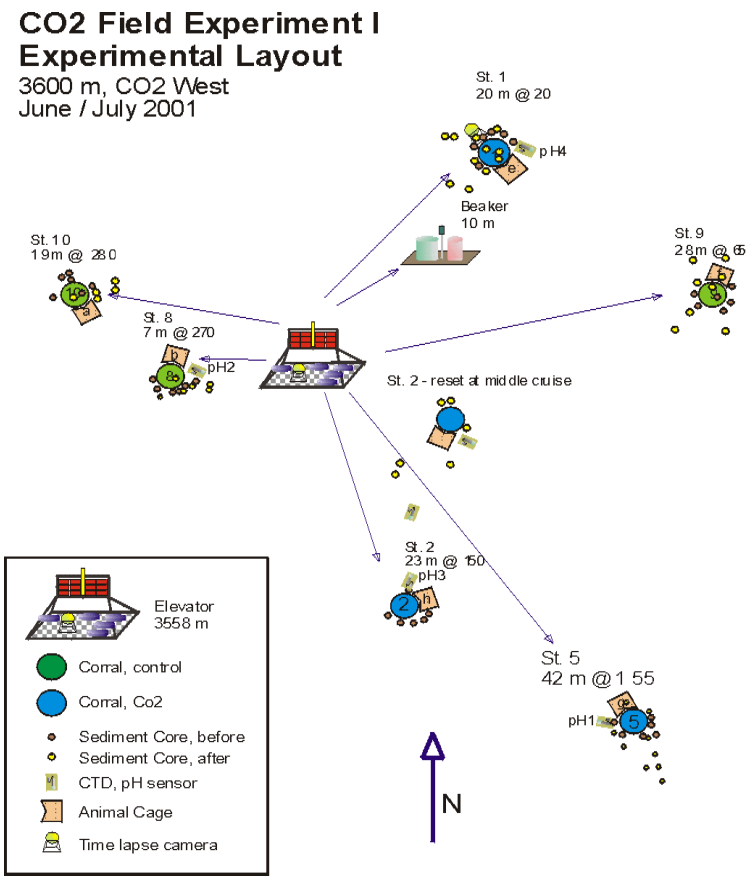


Figure 2. Experimental layout of CO2 field experiment I.

Results

Carbon dioxide exposure

Sensors placed next to the animal cages and CO2 corrals detected sharp reductions in seawater pH periodically, as the prevailing currents oscillated in direction with the semidiurnal tides (Figure 3). pH dropped below 6.0 on several occasions, exposing the nearby seafloor and caged animals to fairly large changes in CO2 and pH.

Megafauna. Mortality of both echinoderm species adjacent to the CO_2 corrals was high, with obvious signs of decalcification of urchin spines and skeletons. Little mortality was detected near control corrals. More detailed physiological examination of these individuals is ongoing.

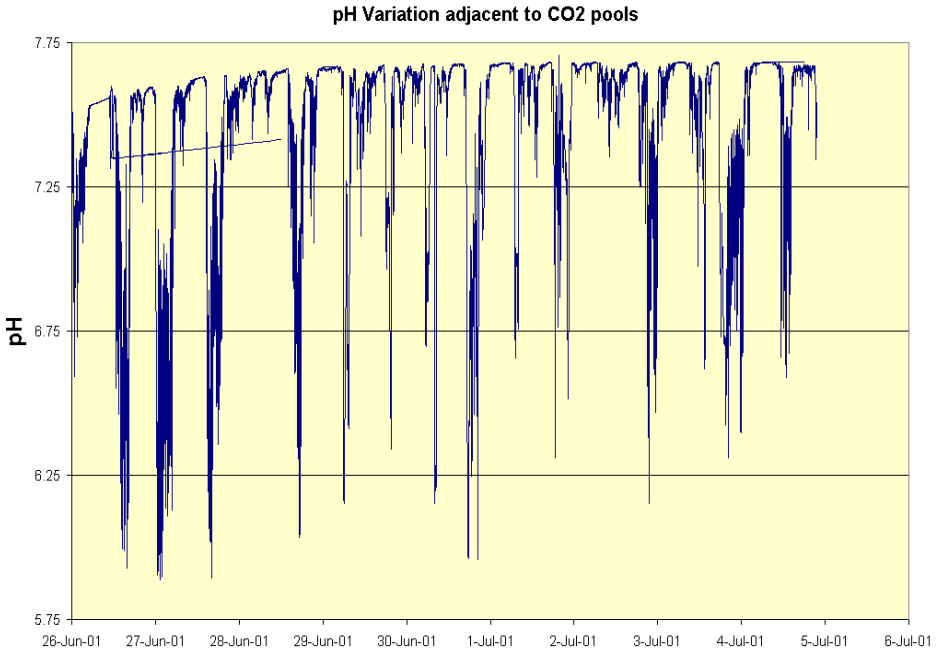


Figure 3. pH variation adjacent to CO2 corrals.

Macrofauna. Amphipod crustaceans are the most abundant macrofaunal groups at the study site, and have shown clear differences in abundance and condition between treatments. Sediments exposed to CO_2 had lower densities of amphipods, with lower gut fullness (reduced feeding) and poorer tissue condition (dead or dying). Differences in other faunal groups have yet to be determined.

Meiofauna. Sample processing is in progress.

Microbial Assemblage. Sample processing in progress.

Although the final results of the experiment require additional laboratory analyses, the experiment was a clear success, replicating the experimental approach incorporating the statistical rigor more typical of shallow water and terrestrial studies.

Deep-sea CO2 Release Experiment II

A second CO_2 release experiment will be performed in October - December 2001 near 3200 m depth off Monterey, CA. In this experiment we will attempt to capture common deep-sea scavenger species (fishes and amphipods) and hold them in cages near and distant from a large CO_2 pool. The duration of the experiment will be approximately 5 weeks. Additional studies, including caging studies similar to Experiment I (above) and measurements of the effects of CO_2 on microbial productivity, are planned in conjunction with the scavenger caging studies.

Laboratory Studies of CO_2 Response

We (Barry and Seibel) have developed a laboratory based respiration system in which we will examine responses of several representative species of deep-sea organisms to CO_2 exposure. Respiration rates typically decrease with exposure to CO_2, due to changes in the transport capacity of respiratory proteins, metabolic depression due to CO_2, or both. We will use the laboratory system to examine differences in CO_2 tolerance and response between shallow- and deep-living species. These studies should reveal details of the physiological adaptations underlying sensitivity to CO_2 exposure.

CONCLUSION

Several conclusions arose from this first year of research on the fundamental science underlying direct CO2 sequestration in the ocean. Concerning the methods developed to examine the chemistry and environmental consequences of CO2 sequestration, we are convinced that much progress can be made using small scale (e.g. 1 to 50 l) releases of liquid CO2. This includes examination of CO2 hydrate formation and dissolution, and measurements of the impacts of reduced pH and elevated CO2 on deep-sea organisms. Because we observed some variation in hydrate formation and dissolution during deep-sea releases on the seafloor, we can only conclude that several factors may interact to influence the physical chemistry of liquid CO2 released on deep-sea sediments. Further study may resolve these processes. Larger-scale experiments would complement our small scale studies. Our first experiments were designed to expose seafloor organisms to fairly large changes in seawater chemistry (pH reduction of 1.0 units). The low survival rates of nearly all organisms exposed to such elevated CO2 during this experiment indicates that impacts to marine biota could be severe very near CO2 injection sites unless release methods are designed to reduce environmental impacts.

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