Project Title: Prototype Design and Testing of a Cabled Free Ocean CO_2 Enrichment (FOCE) System

Sanctuary: Monterey Bay National Marine Sanctuary

Project Coordinators/Participants:
Dr. Peter G. Brewer, MBARI Senior Scientist (Ocean Chemistry)
Mr. William J. Kirkwood, MBARI Associate Director of Engineering
Dr. Edward T. Peltzer, MBARI Senior Research Specialist
Dr. James P Barry, MBARI Associate Scientist (Benthic Ecology)
Mr. Peter Walz, MBARI Senior Research Technician

Project Abstract: We propose to design, build, and test a seafloor sea water CO_2 enrichment system, powered and controlled by the MARS cable, to investigate the impacts of the emerging high-CO_2/lower pH ocean on benthic communities. The system will mimic in many ways technologies long used to investigate the impacts of elevated CO_2 levels on land ecosystems. The essential components are: delivery of CO_2 saturated sea water as a working fluid to a mixing chamber, enrichment of local sea water to the desired higher CO_2 level, provision of a delay loop to allow time for the CO_2-H_2O reaction to occur and the lower pH level to be established, and introduction of the lower pH sea water into a small flume to provide flow control and to expose the sea floor ecosystem to the future ocean conditions. pH sensors and current meters will be incorporated into the system and will provide the real-time information flow to control the system. The components will be deployed, assembled, and tested by MBARI's ROV *Ventana*, which will serve to connect the system to the cable. Essential control software for pH and velocity feedback will be created, and a version has already been tested. These will be short term deployments for technology testing, and all deployed equipment will be recovered upon completion of the tests.

Project Rationale: The invasion rate of atmospheric fossil fuel CO_2 into the surface ocean now exceeds ~1 million tons CO_2/hour, and the ocean has already absorbed some 500 billion tons of CO_2 since the start of the industrial era. The resulting acidification of the ocean is now well established, and a pH drop of 0.3 pH units over pre-industrial is anticipated in the second half of this century. The biogeochemical consequences of this change are now widely debated, and major reports have been issued by SCOR/IOC (Scientific Committee on Oceanic Research/Intergovernmental Oceanographic Commission), the UK Royal Society, and a specially convened NSF-NOAA-USGS workshop. Over 20 years ago, the terrestrial science community wrestled with a similar problem – the impact of elevated CO_2 levels on land plants. It was recognized that enclosed greenhouse studies had severe limitations, and thus Free Air CO_2 Enrichment (FACE) techniques were created; this technology has now been adopted world-wide. We propose to investigate taking a similar, but far more difficult, step for ocean science with the intent of making the tools developed similarly available to the ocean science community worldwide. This is consistent with MBARI's fundamental mission of pairing scientists and engineers for the development of better procedures, systems, and methods. This work has the potential to become adopted as a fundamental technique by many

laboratories and nations investigating the impacts of a high CO_2/lower pH ocean on benthic communities, and requests for the development of this important technology have come from laboratories around the world.

Objectives: The specific objective is to develop a fundamental technique for exposing marine ecosystems to the chemical conditions which will characterize the ocean of the late 21st century so that reasonable predictions can be made. This involves the design, fabrication, and testing of a complex CO_2 enrichment system, which can be monitored in real time by a shore-based control system accessed by a cable to provide power and data flow. The objective is thus technology and technique development using the MARS cable as a test-bed.

Intended Use of Results: The results will be used for scientific publication, and the system specifications, the control software etc. will be made openly available. No commercial use is anticipated.

Procedures: The concept design for the proposed system can be simply described, and it derives from procedures used for decades on land at many sites around the world. No prototype figure is yet available since the design is evolving. An image of a test assembly carried on ROV *Ventana* is shown in Figures 1 and 2 below. For work in 2008, all deployments will be short term and equipment will be deployed, tested, run in test mode for up to one week, and then recovered. The basic elements are:

1) A bladder containing sea water enriched in CO_2 to be used as a working fluid. No pure CO_2 liquid or gas will be discharged, only sea water with elevated CO_2 levels. The quantity of CO_2 used to prepare the enriched sea water will vary, but in all cases will not exceed the 20 liter limit per experiment already permitted for previous work.
2) A pump to meter this fluid into a flow of sea water contained within a tube several meters in length so that the emerging sea water is changed in pH by 0.3 to 0.6 pH units (thus bracketing projected future ocean conditions);
3) A control volume or flume on the sea floor fitted with sensors (CTD, pH, pCO_2, oxygen, velocity) where the exiting fluid is monitored.

The system is to be powered by the MARS cable, and data telemetered to shore where the system will be controlled. We will assemble, deploy and connect the system using MBARI's ROV *Ventana*, and recover the equipment in the same manner.

Collections: Since the focus of this proposal is primarily technique development, it is not critical that specimen collections be made. The area selected is not rich in benthic organisms and sea pens represent the dominant fauna. In practice, we propose to collect some specimens in the exposed area (approximately 1m^2).

Schedule: The project will commence in January 2008, and end in December 2010. We request authorization for this period. Field work for testing of components will begin in May 2008. A fully assembled system will be tested in spring 2009, and periodically during the remainder of the year as needed design changes become clear. All

deployments will be short term (a few days), and all equipment will be recovered at the end of each dive sequence.

Environmental Impacts: The environmental impacts of locally lowering the pH of sea water by 0.3 to 0.6 pH units are expected to be subtle. Changes of this scale naturally occur in surface ocean waters with seasonal upwelling and have done so for millennia. Many deep-sea animals vertically migrate through gradients larger than this (pH surface ~ 8.1; pH at a few hundred meters ~ 7.6) daily. The pH altered sea water region created for these experiments will return to normal levels within seconds. Thus our experiments would not be expected to show significant short term impacts. The area impacted by the discharge within detectable limits will not exceed a 3-meter-diameter circle. The sea floor area on which we deploy is expected to return rapidly to its normal state.

Products: All information obtained will be freely available for public use.

Publications and Reports: We anticipate numerous publications and reports, but we cannot be more specific at this time.

Data and Other Materials: The system specifications and control software that will be generated will be freely available. Video material obtained during the course of the experiments will be archived at MBARI and maintained as part of the Institutional archival and data base activities.

Literature Cited: No literature has been cited in the pages above. However relevant reading includes:

Andersen, N.R. and A. Malahoff (1977) The Fate of Fossil Fuel CO_2 in the Oceans. Plenum Press, 749 pp.

Cicerone, R., J. Orr, P.G. Brewer, P. Haugan, L. Merlivat, T. Ohsumi, S. Pantoja, and H.O. Poertner (2004) The ocean in a high CO_2 world. *Eos*, **85**, 351-353.

Brewer, P.G., E.T. Peltzer, P. Walz, I. Aya, K. Yamane, R. Kojima, Y. Nakajima, N. Nakayama, P. Haugan, T. Johannessen. (2005) Deep Ocean Experiments with fossil fuel carbon dioxide: creation and sensing of a controlled plume at 4 km depth. *J. Mar. Res*., **63**, 9-33.

Dunk, R.M., E.T. Peltzer, P. Walz, P.G. Brewer (2005) Seeing a Deep Ocean CO_2 Enrichment Experiment in a New Light: Laser Raman Detection of Dissolved CO_2 in Seawater. *Environ. Sci. Technol.*, **39**, 9630-9636.

Kita, J. and T. Ohsumi (2004) Perspectives on biological research for CO_2 ocean sequestration. *J. Oceanogr.*, **60,** 695-703.

Kurihara, H. and Y. Shirayama (2004) Effects of increased atmospheric CO_2 on sea urchin early development. *Mar. Ecol.-Prog. Ser.*, **274**, 161-169.

Langdon, C. and others (2002) Review of experimental evidence for effects of CO_2 on calcification of reef builders. Proc. 9th Int. Coral Reef Sym., 2, 1091-1098.

NSF-NOAA-USGS (2006) Impacts of ocean acidification on coral reefs and other marine calcifiers. Report of a Workshop. J.A. Kleypas, R.A. Feely, V.J. Fabry, C. Langdon, C.L. Sabine, and L.L. Robbins, Eds.

Peltzer, E.T., P.G. Brewer, R.M. Dunk, M.P. Fuchs, P.M. Walz (2006), Deep Ocean CO_2 Hydration Kinetics, Eos. Trans. AGU 87(36) Ocean Sci. Meet. Suppl., Abstract OS45B-20.

Royal Society, Ocean acidification due to increasing atmospheric carbon dioxide, pp. 60, 2005.

Tamburri, M., E.T. Peltzer, G. Friederich, I. Aya, K. Yamane, and P.G. Brewer. (2000) A field study of the effects of CO_2 disposal on mobile deep-sea animals. *Mar. Chem.*, **72**, 95-101.

US Dept. Of Energy (1985) Direct effects of increasing carbon dioxide on vegetation. Report # DOE/ER-0238. B.R. Strain and J.D. Cure, Eds.

Zeebe, R.E. and D. A. Wolf-Gladrow (2001) *CO_2 in Seawater: Equilibrium, Kinetics, Isotopes*, Elsevier Oceanogr. Ser., **65**, 345 pp., Elsevier, New York.

Qualifications:

Peter G. Brewer

a. Professional Preparation.

B.Sc., Liverpool University, England, 1962; Ph.D., Liverpool University, England, 1967.

b. Appointments.

Senior Scientist, Monterey Bay Aquarium Research Institute (MBARI), 1996 - present.
President and Chief Executive Officer, MBARI, 1991-1996.
"By Courtesy" Professor, Stanford University – School of Earth Sciences, 1991-present.
Senior Scientist, Woods Hole Oceanographic Institution, 1978-1991.
Program Director, Marine Chemistry, National Science Foundation, 1981-1983.
Associate Scientist, Woods Hole Oceanographic Institution, l971-1978.
Assistant Scientist, Woods Hole Oceanographic Institution, 1967-1971.

AWARDS

- Fellow, American Geophysical Union.
- Fellow, American Association for the Advancement of Science.
- National Science Foundation, Sustained Superior Performance Award.

c. 5 Closely Related Publications

Brewer, P.G. (2007) Evaluating a technological fix for climate. *Proc. Natl. Acad. Sci.*, 104, 9915-9916.

Thistle, D., L. Sedlacek, K.R. Carman, J.W. Fleeger, P.G. Brewer, J.P. Barry (2007) Exposure to carbon dioxide-rich seawater is stressful for some deep-sea species: an in situ, behavioral study. *Mar. Ecol. Progr. Ser*., **340**, 9-16.

Dunk, R.M., E.T. Peltzer, P. Walz, P.G. Brewer (2005) Seeing a Deep Ocean CO_2 Enrichment Experiment in a New Light: Laser Raman Detection of Dissolved CO_2 in Seawater. *Environ. Sci. Technol.*, **39**, 9630-9636.

Caldeira, K., M. Akai, P. Brewer, B. Chen, P. Haugan, T. Iwama, P. Johnston, H. Kheshgi, Q. Li, T. Ohsumi, H. Poertner, C. Sabine, Y. Shirayama, and J. Thomson (2005) Ocean Storage. In: *(B. Metz and O. Davidson, eds.) Carbon Dioxide Capture and Storage: A Special Report of IPCC Working Group II*I, Cambridge University Press, Cambridge UK.

Brewer, P.G., E.T. Peltzer, P. Walz, I. Aya, K. Yamane, R. Kojima, Y. Nakajima, N. Nakayama, P. Haugan, T. Johannessen. (2005) Deep Ocean Experiments with fossil fuel carbon dioxide: creation and sensing of a controlled plume at 4 km depth. *J. Mar. Res.*, **63**, 9-33.

5 Other significant publications

Cicerone, R., J. Orr, P.G. Brewer, P. Haugan, L. Merlivat, T. Ohsumi, S. Pantoja, and H.O. Poertner (2004) The ocean in a high CO_2 world. *Eos*, **85**, 351-353.

Nakayama, N., E.T. Peltzer, P. Walz, P.G. Brewer. (2005) First results from a controlled deep-sea CO_2 perturbation experiment: evidence for rapid equilibration of the oceanic CO_2 system at depth. *J. Geophys. Res.*, **110**, C09S11, doi:10.1029/2004JC002597.

D. Thistle, L. Sedlacek, K. R. Carman, J. W. Fleeger, P. G. Brewer, and J. P. Barry (2006) Simulated sequestration of industrial carbon dioxide at a deep-sea site: effects on harpacticoid-copepod species. *J. Exp. Mar. Biol. Ecol.*, **330**, 151-158.

Brewer, P. G., B. Chen, R. Warzinski, A. Baggeroer, E. T. Peltzer, R. M. Dunk, and P. Walz (2006), Three-dimensional acoustic monitoring and modeling of a deep-sea CO_2 droplet cloud, *Geophys. Res. Lett.*, **33**, L23607, doi:10.1029/2006GL027181.

d. Synergistic Activities.

Dr. Brewer has long been involved in professional and scholarly activities of broad benefit to the scientific community. Activities include:

- Service as Chair of the U.S. JGOFS Program, and Vice-Chair of JGOFS.
- Service on numerous committees of the National Research Council, including the Pacific Science Association with its mission to encourage science in the Pacific Island Nations.

- Co-Chair of the NSF OCE Decadal Report "Ocean Sciences at the New Millennium".
- Leadership in establishing ocean CO_2 sequestration science and representation for the U.S. on IPCC WG III Special Report on Carbon Capture and Storage (2005).
- Committees of the American Geophysical Union, including Chairing the Editorial Search for Geophysical Research Letters, and serving on the Flinn Award Committee.
- Co-Chair of the ICES Working Group on Ocean Acidification.

e. Collaborators & Other Affiliations
Collaborators and Co-Editors (previous 48 months):
Post-Doctoral Advising: John Ryan (URI, now at MBARI), Gregor Rehder (IfM-GEOMAR, Kiel, Germany), Sheri White (WHOI-MIT), Rachel Dunk (York Univ., UK), Noriko Nakayama (U. Tokyo), Keith Hester (CSM)
Collaborators: E. Adams (MIT), M. Akai (AIST), G. Alendal (U. Bergen), I. Aya (NMRI), A. Baggeroer (MIT), R. Bellerby (U. Bergen), K. Caldeira (Carnegie Inst), K. Carman (LSU), B. Chen (AIST), R. Cicerone (NAS), W. Durham (LLNL), R. Gangsto (U. Bergen), P. Haugan (U. Bergen), K. Hester (CSM), T. Iwama (Seinan U.), T. Johannessen (U. Bergen), S. Kirby (USGS), R. Kleinberg (Schlumberger), L. Merlivat (U. Paris), Y. Nakajima (NMRI), T. Ohsumi (CRIEPI), S. Pantoja (Chile), J. Pasteris (Washington U.), H. Poertner (U. Bremen), C. Sabine (NOAA-PMEL), T. Sato (U. Tokyo), Y. Shirayama (U. Kyoto), E. Sloan (CSM), L. Stern (USGS), D. Thistle (FSU), C. Tsouris (ORNL), R. Warzinski (NETL), B. Wopenka (Washington U.), K. Yamane (NMRI), J. Yesinowski (NRL).

William J. Kirkwood
a. Professional Preparation.
BSME, University of California Los Angeles, 1979; MSCIS, University of Phoenix, 2000.

b. Appointments.

National Science Foundation, Ocean Observatory Initiative ORION Office, Engineering Committee (2006)

Santa Clara University: Appointed Adjunct Professor - since Fall 2002

c. Closely Related Publications

Walz, P.M., Brewer, P.G., Peltzer, E.T., Dunk, D.M., Graves, D., Scholfield, J., Kirkwood, W., (2006) "Free Ocean Carbon Dioxide Enrichment (FOCE): Control and Measurement of Ocean Saewater to Simulate a Low pH-High CO2 Ocean" *ASLO / TOS / AGU Ocean Sciences Meeting*, Honolulu, Hawaii, February 20-24, 2006, OS15D-12.

Kirkwood, W., D. Graves, M. Conway, D. Pargett, J. Scholfield, P. Walz, R. Dunk, E. Peltzer, J. Barry, and P. Brewer (2005)"Engineering Development of the Free Ocean

CO2 Enrichment (FOCE) Experiment" *MTS/IEEE Oceans 2005*, Washington D.C., October 2005, MTS/IEEE #050304-93.

5 Other significant publications

Sheri N. White, William Kirkwood, Alana Sherman, Mark Brown, Richard Henthorn, Karen Salamy, Peter Walz, Edward T. Peltzer, and Peter G. Brewer (2005), "Development and Deployment of a Precision Underwater Positioning System for In Situ Laser Raman Spectroscopy in the Deep Ocean" *Deep Sea Research, Vol 5, No. 1,* Ms. Ref. No.: DSR1-D-05-00037R1.

Caress, D. W., Kirkwood, W. J., Thomas, H., McEwen, R., Henthorn, R., McGill, P., Thompson, D., Sibenac, M., Jensen, S., Shane, F., Hamilton, A., (2005) "MBARI Mapping AUV: A High-Resolution Deep Ocean Seafloor Mapping Capability" *AGU 2005 Joint Assembly*, May 23-27, 2005, New Orleans, LA. #U24A-02.

S. N. White, Kirkwood, W., M. Brown, R. Henthorn, S. Jensen, K. A. Salamy, E. T. Peltzer, and P. G. Brewer (2004), "Laser Raman Spectroscopic Instrumentation for in situ Geochemical Analyses in the Deep Ocean." *MTS/IEEE Oceans 2004*, Kobe, Japan. MTS/IEEE #470.

Tervalon, N. & Kirkwood, W., "Ice Profiling Sonar for an AUV: An approach for obtaining SCICEX quality ice draft data", Oceanology International - Amercias Conference, AUV Sensor Workshop Proceedings, Miami, Florida, April 2001.

Kirkwood, W., Bellingham, J., Stannard, J., Stein, P., Overland, J., "Development of Dorado / ALTEX Vehicle and Subsystems**",** Society for Underwater Technology - AUV Masterclass Symposium Proceedings, Southampton Oceanographic Centre, Southampton, England, September 2001.

d. Synergistic Activities.

Mr. Kirkwood has worked on the problem of ocean acidification and the associated technology with Dr. Brewer and his colleagues for over 5 years. Mr. Kirkwood has successfully developed prototype systems for *in situ* science to study pH changes due to anthropogenic CO_2 as well as other ocean chemistry questions. Mr. Kirkwood has attended numerous science conferences and ocean acidification workshops to bring forward new technologies and capabilities to the ocean science community such as deep sea corals as outlined in the 2006 NOAA report on Ocean Acidification.

e. Collaborators & Other Affiliations

Collaborators and Co-Editors (previous 48 months):

Post-Doctoral Assistance: Sheri White (WHOI-MIT), Rachel Dunk (York Univ., UK), Noriko Nakayama (U. Tokyo), Keith Hester (CSM), Nicole Tervlaon (MIT).

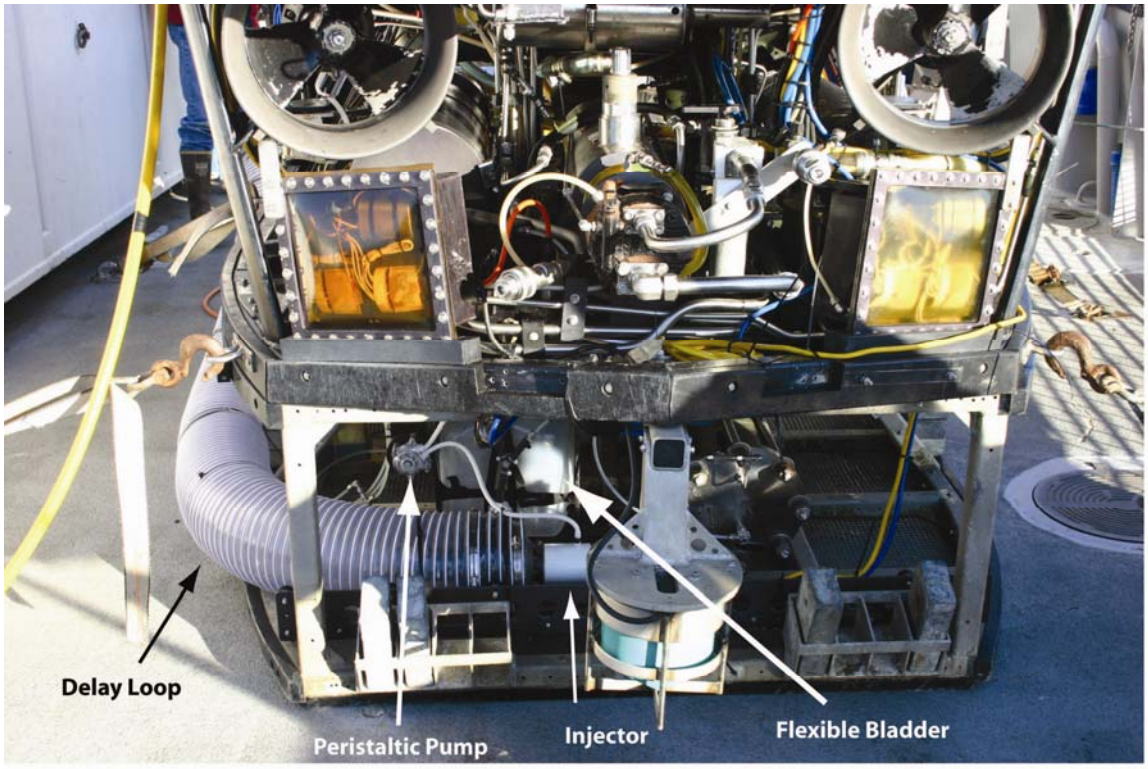

Figure 1. Rear view of ROV *Ventana* showing the placement of the peristaltic pump for precisely adding small quantities of CO_2-enriched seawater into the front end of the delay loop.

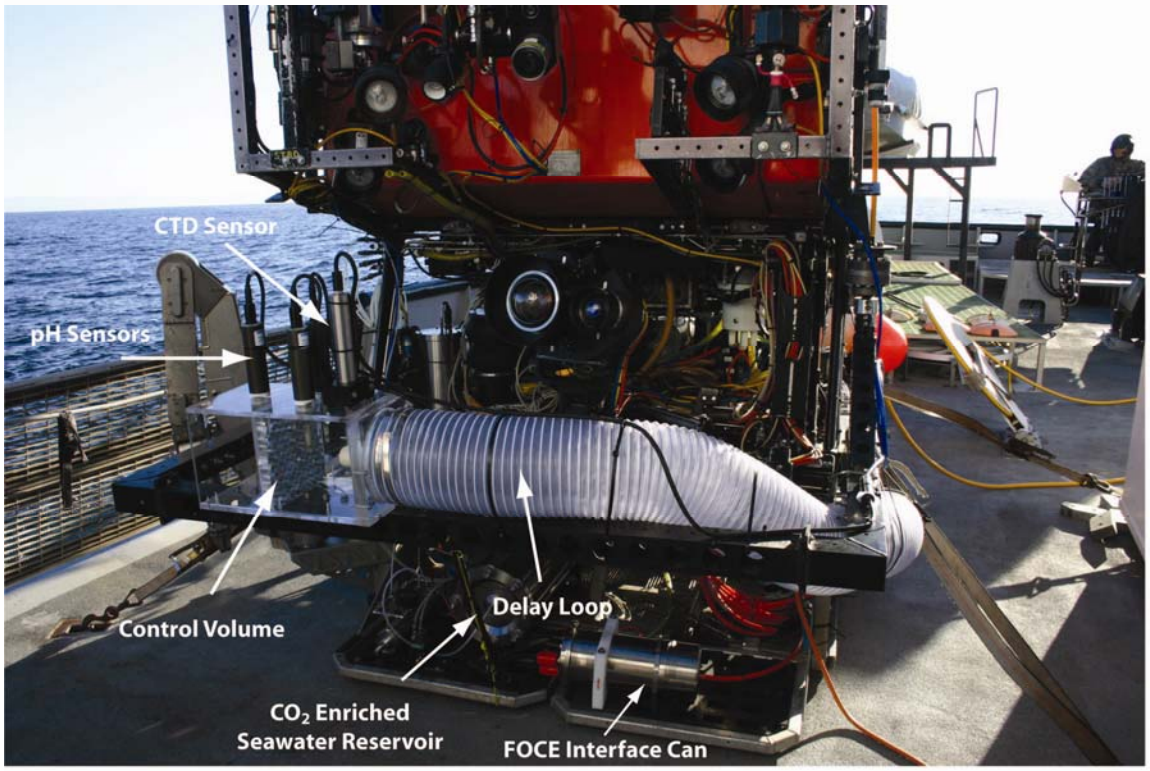

Figure 2. Front view of ROV *Ventana*, showing the control volume with 3 pH sensors and a CTD sensor at the outlet of the delay loop.