

**OCEAN ACIDIFICATION WORKSHOP**  
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**POSTER ABSTRACTS**

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**Carbonate Dissolution in Shallow Water Carbonate Platform Sediments**

We have estimated carbonate dissolution rates for sediments on the Bahamas Bank using an inverse pore water advection/diffusion/reaction model applied to pore water O<sub>2</sub>, alkalinity, and DIC profiles. The sites we have studied include ooid sands, grapestone deposits, and aragonite muds, with a wide range of seagrass densities. Integrated rates of carbonate dissolution at these sites (i.e., dissolution fluxes) range from <2 mmol m<sup>-2</sup> d<sup>-1</sup> (ooid sands with no seagrass coverage) to ~80 mmol m<sup>-2</sup> d<sup>-1</sup> for sediments underlying dense seagrass beds. These carbonate dissolution fluxes are also positively correlated with seagrass density. In part this occurs because sub-surface pumping of photosynthetically-produced O<sub>2</sub> from seagrass roots and rhizomes is a major driver of benthic aerobic respiration (and hence metabolic carbonate dissolution) in these sediments.

Using our results, dissolution fluxes integrated over the entire Bahamas Bank are ~3 mol m<sup>-2</sup> yr<sup>-1</sup>, and are of similar magnitude to gross carbonate production fluxes (~5 mol m<sup>-2</sup> yr<sup>-1</sup>). When the carbonate dissolution rates estimated here are examined in the context of carbonate budgets for shallow water carbonate platforms, they suggest that carbonate dissolution may be a significant loss term in these budgets. Furthermore, depending on the magnitude of offshore transport of platform carbonates, these results also raise important question about the steady-state nature of these carbonate budgets.

The occurrence of coupled dissolution/precipitation may impact the way in which shallow water HMC acts as a buffer for rising atmospheric CO<sub>2</sub>, depending on whether the solubility and/or kinetic reactivity of the secondary phase differs significantly from that of the initial phase. Given the dynamics of these processes, the seagrass-mediated carbonate dissolution we have observed may also exert a negative feedback on rising atmospheric CO<sub>2</sub>, although the magnitude of this effect remains to be quantified.

**Dunne, J. P., and J. R. Toggweiler**

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**Implementation of calcium carbonate cycling and ocean acidification parameterization in global models**

As anthropogenic CO<sub>2</sub> is changing ocean chemistry, it is imperative that global models implement a mechanistically sound representation of CaCO<sub>3</sub> cycling in coupled carbon-climate models of centennial prediction in order to address three critical questions: How will CO<sub>2</sub> invasion respond to ocean acidification through alteration of the CaCO<sub>3</sub> cycle? How will ocean acidification impact calcifying organisms? And, how will the impacts to calcifiers and other acidification-sensitive biota resound through marine ecosystems? We provide a review of global scale fluxes associated with the CaCO<sub>3</sub> cycle as it is currently understood, description of the mechanisms thought to control CaCO<sub>3</sub> cycling, and the current status of modeling efforts towards developing mechanistic parameterizations of these process. Our hope is to use this as a basis for a larger community discussion to assess potential directions and the level of community consensus with respect to predicting future anthropogenic CO<sub>2</sub> uptake, assessing the impact of ocean acidification on CaCO<sub>3</sub> cycling in particular and ecosystems as a whole, and quantifying the sensitivity of model predictions to uncertainties in model parameterizations.

**Färber Lorda, J.<sup>1</sup>, and P. Fiedler<sup>2</sup>**

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**Day-Night Differences In Zooplankton Biomass In The Eastern Tropical Pacific. Results From Historical Data**

According to our recent results in the eastern tropical Pacific (ETPac), no day-night differences in near surface (0-200m) zooplankton biomass have been found during summer or winter cruises (Färber-Lorda et al., 2004b, Färber-Lorda et al., 2004c and Fernandez-Alamo and Färber Lorda, 2006). Trying to better understand these results and considering the special features of this wide area; we examined historical data to determine whether these differences were real or just the consequence of limited or too variable data. Historical data from the EASTROPAC cruises and other cruises were utilized. An ANOVA comparing night and day zooplankton volumes obtained with a 330 µm mesh net, showed significant differences. Other statistical tests separating season, or bimester showed significant differences with a multiple way ANOVA. Even if significant differences were found, probably due to the great variability of the results, large areas of the ETPac show a night/day zooplankton volume ratio close to 1, these are areas, in general characterized by a shallow oxygen minimum layer (40 -100m), in which oxygen is lower than 1 ml/l, and cover a wide area in the northern hemisphere between 5 to 15° N and around the Costa Rica Dome. A smaller set of data of samples obtained with a 505 µm mesh net, also showed significant differences. It is hypothesized that low oxygen is limiting the vertical migration of zooplankton.

A comparison with the California Current zooplankton volume data from the CalCOFI program, showed no differences for samples obtained with a 505 µm mesh net, night/day ratios seem to be higher in the ETPac, however, night/day ratios of less than 1 were very almost absent in the CalCOFI area. Further studies are in course to better understand this phenomenon.

References

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**Gattuso, Jean-Pierre, and the EPOCA consortium**

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**European Project on Ocean Acidification (EPOCA)**

The *European Project on Ocean Acidification* (EPOCA) has been favorably evaluated by the European Commission and will probably start in early 2008. EPOCA's overall goal is to advance our understanding of the biological, ecological, biogeochemical, and societal implications of ocean acidification. It's research efforts are divided into four research themes. First, EPOCA will focus on past and present spatiotemporal changes in ocean chemistry and biogeography of key marine organisms. Archives of foraminifera and deep-sea corals will help determine past variability in ocean chemistry (carbonate, nutrients, and trace metals). Those will be linked to present-day chemical and biological observations. Second, EPOCA will help quantify impacts of ocean acidification on marine organisms and ecosystems. EPOCA will use a range of techniques, from molecular tools to physiological and ecological approaches, to study climate-relevant biogeochemical processes, including calcification, primary

production, and nitrogen fixation. Laboratory and field perturbation experiments will focus on key organisms in terms of their ecological, biogeochemical, or socioeconomic importance. Third, EPOCA will improve biogeochemical, sediment, and coupled ocean-climate models to better account for how ocean acidification will affect ocean biogeochemistry and ecosystems. Special attention will be paid to feedbacks of physiological changes on the carbon, nitrogen, iron, and sulfur cycles and in turn how these changes will affect and be affected by future climate change. Finally, EPOCA will assess uncertainties, risks, and thresholds (tipping points) related to ocean acidification at molecular, cellular, and organismal levels from local to global scales. We will identify the CO<sub>2</sub> emission pathways that are required to avoid these thresholds, and if exceeded, the potential consequences to the marine environment and Earth system. Our success depends on efficiently combining the strengths of the EPOCA consortium of 28 partner institutes, including 105 principal investigators. EPOCA will coordinate with major national and international projects and programs. The requested financial contribution from the Commission of 7 M€ is complemented by outside funds of another 10 M€. EPOCA's success also depends on developing strong links with the US community. Four US scientists (K. Caldeira, V. J. Fabry, R. A. Feely, and J. A. Kleyvas) are included on the EPOCA International Advisory Board.

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### **Ocean Acidification of the Greater Caribbean Region 1996 – 2006**

The global oceans serve as the largest natural sink for increasing atmospheric carbon dioxide (CO<sub>2</sub>) concentrations. As this CO<sub>2</sub> is absorbed by seawater, it reacts to form bicarbonate and hydrogen ions resulting in a reduction in seawater pH (or acidification). This results in a decrease in the availability of the carbonate ion which has been demonstrated to play an important role in calcification for a number of marine organisms. Ocean acidification could affect some of the most fundamental biological and geochemical processes of the sea in coming decades. Observations obtained *in situ* from Volunteer Observing Ships have been extended using satellite remote sensing and modeled environmental parameters to derive estimates of sea surface alkalinity (A<sub>T</sub>) and surface carbon dioxide partial pressure (pCO<sub>2,sw</sub>). Pairing estimates of A<sub>T</sub> and pCO<sub>2,sw</sub> has permitted characterization of the changes in sea surface carbonate chemistry that have transpired over the past decade throughout the Greater Caribbean Region as a consequence of ocean acidification. The results reveal considerable variability both spatially and seasonally throughout the region. As a consequence of ocean acidification, a secular decrease in aragonite saturation state (Ω<sub>arg</sub>) is observed at a rate of ~ -0.12 ± 0.01 Ω<sub>arg</sub> decade<sup>-1</sup> (r<sup>2</sup> = 0.97, P < 0.0001).

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### **Active pCO<sub>2</sub>-Control of Seawater Culture Systems for Laboratory-Based Biogeochemical Experimentation Investigating Global Ocean Acidification**

The large-scale effects of anthropogenic CO<sub>2</sub> rise and global ocean acidification on calcifying and photosynthetic organisms are not well understood. This ongoing uncertainty fundamentally limits our ability to fully understand global carbon cycling. Field-based studies are limited to the current environmental chemistries observed throughout the world's oceans – a prohibitively resource-intensive platform for manipulative experimentation. Moreover, complex carbonate system equilibria decoupled from the atmosphere are difficult to poise and maintain in laboratory seawater-based experiments lasting longer than a few hours or days. This severely limits the scope of biogeochemical experimentation for simulating past or future ocean chemistries.

To address these experimental shortcomings I developed a novel system for the stringent control of pCO<sub>2</sub> in culture aeration and seawater. A custom CO<sub>2</sub> scrubbing system was designed which removes > 99.8% of atmospheric CO<sub>2</sub> at 3-4 L min<sup>-1</sup> aeration rate. High precision mass flow controllers integrated with a modular programmable process controller precisely mix high-purity (99.95%) compressed CO<sub>2</sub> with the preconditioned CO<sub>2</sub>-free air stream for aeration into the culture system. Long-term maintenance of experimental CO<sub>2</sub> is within ± 2 μatm when operating between 150-2000 μatm pCO<sub>2</sub>. The system, in its current configuration, has the ability to simultaneously manipulate and maintain 3 separate carbonate chemistries using aeration pCO<sub>2</sub> and seawater alkalinity in independent 400-L seawater reservoirs. Future system expansion can easily maintain 5 or more separate chemistries.

The goal of this research is to develop stringent control of seawater carbonate system chemistries for the Deep-Sea Benthic Foraminifera Culture Facility housed at the University of South Carolina Arnold School of Public Health. Current experiments are investigating trace metal foraminiferal paleoproxy signatures that appear correlated with [CO<sub>3</sub><sup>2-</sup>] very near calcite saturation. My system's control of equilibrium pCO<sub>2</sub> allows precise maintenance of the culture's carbonate system chemistry very near, above and below calcite saturation, while maintaining realistic values for alkalinity and dissolved inorganic carbon. I gratefully acknowledge the funding for this research by the University of South Carolina Arnold School of Public Health and the National Science Foundation - OCE 0647891, and travel assistance to this workshop by the Ocean Acidification Workshop Steering Committee and the National Science Foundation's Office of Polar Programs.

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### **Early Detection of Ocean Acidification Effects on Marine Calcification at a Global & Ecosystem Scale**

Ocean acidification is likely to impact calcification rates in many pelagic organisms, which may in turn cause significant changes in marine ecosystem structure. We examine changes in marine CaCO<sub>3</sub> production using the global biogeochemical ocean model HAMOCC in combination with observational data. Calcification in different organisms shows a wide range of sensitivities to saturation state. Therefore, we test different future calcification scenarios. The model integrations start at a pre-industrial steady state in the year 1800 and run until the year 2300 forced with anthropogenic CO<sub>2</sub> emissions. Model results are evaluated taking into account the natural variability in ocean carbonate chemistry.

Using a synthesis of modeling and observational data, we address the following questions. (1) At what time does ocean acidification lead to a decline in marine calcification on a global scale that is detectable in the data? (2) Assuming different calcification scenarios, does the data presently available already allow discerning significant trends, given natural variability and data uncertainties? (3) If so, what is the magnitude and time scale of the decline? Our long-term goal is to help identifying target regions for future ocean chemistry surveys that are critical for early detection and determination of the exact magnitude of large-scale acidification effects from field data.

**Kirkwood, William J., Edward T. Peltzer and Peter G. Brewer**

MBARI

### **In Situ Ocean Acidification Environmental Observations: MBARI's Cabled Observatory Technology for Controlled Studies of Changing Ocean pH**

This poster explores modifications to the design, fabrication and implementation of the field tested prototype Free Ocean CO<sub>2</sub> Enrichment (FOCE) system. The proof of concept prototype system was able in the field to control pH perturbations from acid release simulating CO<sub>2</sub> induced pH changes in specific habitat experiments. The acidified flow was pumped so as to maintain a constant delta pH under varying

environmental conditions. The modified FOCE system concept is to be powered and supplied by a cable and pipe system from shore, and to move towards CO<sub>2</sub>-rich water rather than acid releases. Discussion of the FOCE test results to date indicates paths to improved performance, with a primary problem being system design to accommodate the slow kinetics of the CO<sub>2</sub> hydration reaction in sea water. This paper discloses current MBARI science and engineering efforts and concepts towards an ocean observing system solution by integrating the chemical kinematics of the CO<sub>2</sub>–water reaction and the next step in FOCE development for in situ science.

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### **The sensitivity of corals, coccolithophorids and foraminifera to carbonate ion concentration – a synthesis**

For the purposes of comparing the sensitivity of corals, coccolithophorids and foraminifera to a change in carbonate ion concentration or saturation state it is convenient to normalize the calcification rates to the rate at some defined concentration or saturation state. This has the benefit of removing the variability in absolute rates between different organisms and allows one to see the underlying similarity or dissimilarity in the response. The sensitivity of twelve species of coral to a change in [CO<sub>3</sub><sup>2-</sup>] or [Ca<sup>2+</sup>] has been examined. The data reveal some diversity in the response. One early study reported that calcification increased with increasing aragonite saturation state ( $W_a$ ) up to a value of 3.0 and then remained constant up to a value of 6.0. The bulk of the subsequent studies suggest a linear relationship that goes to zero at  $W_a=1.0$  and has a slope of 22-28% per unit change in  $W_a$  (Fig. 1). The massive coral *Porites lutea*, widely used in paleo-climatological studies, is among this group of species exhibiting a strong, linear dependence on saturation state. There is a group of three species that exhibit a much weaker dependence of 6-9% per unit change in  $W_a$ . A linear regression through the data from all available studies gives  $G = -0.45 + 22.7(W_a)$ ,  $r^2=0.67$ , where  $G$  is the calcification rate as a percentage of the pre-industrial rate. The first-order rate law  $G=27.8(W_a-1)$  gives an equally good fit to the data. If rates are regressed against [CO<sub>3</sub><sup>2-</sup>] the relationship has a slope of 36% per 100 mmol kg<sup>-1</sup>. Coccolithophorids exhibit wide range of dependences on [CO<sub>3</sub><sup>2-</sup>] from positive to an optimum at present day [CO<sub>3</sub><sup>2-</sup>] to negative. Forams exhibit a weaker dependence on [CO<sub>3</sub><sup>2-</sup>] than corals over most of the range in [CO<sub>3</sub><sup>2-</sup>] but with only two species studied it is difficult to generalize.

**Martz, Todd R., Hans W. Jannasch and Kenneth S. Johnson**

Monterey Bay Aquarium Research Institute

### **Determination of carbonate ion by spectrophotometric titration**

We describe a novel method for determination of carbonate ion concentration in seawater by acidimetric titration with UV detection. Because CO<sub>3</sub><sup>2-</sup> absorbs light at wavelengths of less than ~250 nm, it is feasible to titrate seawater with acid and observe an increase in %Transmittance. The observed signal is proportional to the concentration of carbonate ion in the original sample. The procedure has been tested at 1 and 10 cm pathlengths using single and multipoint titration methods. Preliminary results using real and artificial seawater test solutions indicate a resolution in [CO<sub>3</sub><sup>2-</sup>] of ~ 6 μM (1 σ) in a standard 1cm cuvette using a very simple manual method, and ~ 1.3 μM (1 σ) using a custom built 10 cm closed titration cell. We are currently refining the analysis method for multipoint titrations and addressing issues related to standardization. Proper standardization requires quantification of the effects of seawater media on CO<sub>3</sub><sup>2-</sup> molar absorptivity and method response to changes in the ratio of [CO<sub>3</sub><sup>2-</sup>]<sub>free</sub> to [CO<sub>3</sub><sup>2-</sup>]<sub>total</sub>. This method provides a new tool for studies of several fundamental aspects CO<sub>2</sub> chemistry, including the second dissociation constant of carbonic acid, CO<sub>3</sub><sup>2-</sup> ion pairing, and could be used to directly measure the distribution of carbonate ion in seawater.

**Peltzer, Edward T., Peter G. Brewer, Rachel M. Dunk, Megan P. Fuchs and Peter M. Walz**  
MBARI

### **Deep Ocean CO<sub>2</sub> Hydration Kinetics.**

The slow hydration / de-hydration kinetics of carbon dioxide at ambient temperatures and pressures are well known to ocean chemists. Johnson (1982) reported the rate constant for the hydration reaction in seawater as a function of temperature. More recently, Zeebe and Wolf-Gladrow (2001), have compiled a comprehensive model of these kinetics, which illustrate the strong impact of pH on reaction rate. In our recent studies of CO<sub>2</sub> dissolution in seawater as part of an ocean CO<sub>2</sub> sequestration scenario, we have observed a significant under-estimation of total CO<sub>2</sub> concentrations when pH alone is used in close proximity to the CO<sub>2</sub> source. For similar reasons, we anticipate analogous errors when measuring the total CO<sub>2</sub> concentrations at close proximity to sea-floor CO<sub>2</sub> vents on the flanks of undersea volcanoes. At the same time, preliminary measurements of CO<sub>2</sub> hydration kinetics at low temperature but elevated pressures (such as would be encountered at CO<sub>2</sub> sequestration sites or CO<sub>2</sub> vents on the flanks of seafloor volcanoes), have suggested that pressure may be inducing enhanced reaction rates. In order to test this hypothesis, we have begun a systematic study of CO<sub>2</sub> hydration rates in the deep ocean using MBARI's advanced ROV technology.

We have attempted to study the effects of temperature (T=5-20°C), pressure (P=0-1000 dbar), and size of perturbation ( $\Delta\text{pH} = \text{pH}_{\text{initial}} - \text{pH}_{\text{final}} = 0.1-0.6$ ) on CO<sub>2</sub> hydration kinetics. A small volume (1ml) of dilute hydrochloric acid is injected into 500ml of seawater contained in a continuously circulating reaction chamber. Immediately next to the injector the pH drops precipitously, driving the carbonate equilibria to the left and momentarily generating a small parcel of seawater where the bulk of the carbon dioxide is in the form of the dissolved gas molecule. This high CO<sub>2</sub>-low pH parcel is rapidly mixed (~5sec) with the ambient pH seawater, and the measured pH increases. The CO<sub>2</sub> then slowly hydrates, generating hydrogen ions and lowering the pH. From the measured exponential drop in pH, we are able to determine the reaction relaxation time. The results of these experiments will be presented and compared with the Johnson (1982) and Zeebe and Wolf-Gladrow (2001) models as a function of T, P and  $\Delta\text{pH}$ .

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### **Florida Shelves: Natural Laboratories to Study Community Response to Ocean Acidification**

Declining oceanic pH and carbonate-ion concentrations are potential consequences of increased atmospheric and surface-ocean pCO<sub>2</sub>. The possible impact of shifts in seawater carbonate chemistry on biocalcification and survival rates of marine organisms are pressing questions that are amenable to field study. The continental shelves of Florida provide an ideal natural laboratory in which to test latitudinal (and depth) shifts in habitat ranges of calcifying organisms. For example, the west Florida shelf extends from warm temperate to subtropical latitudes. Along this gradient, carbonate sedimentation changes from predominantly animal-produced shell hashes known as “heterozoan” carbonates that accumulate at rates of centimeters per 1000 years, to subtropical reef environments where “photozoan” carbonate sediments are produced in association with photosynthesis, at rates that can exceed a meter per 1000 years (i.e., hypercalcification). Changes in either latitudinal or depth distributions of these benthic assemblages on

the Florida shelves would provide convincing evidence of ecosystem-level effects of ocean acidification on calcifying organisms.

A USGS-USF study is documenting potential shifts in latitudinal distributions and vertical depth ranges of larger foraminifera, mollusks, and calcifying algae as the CO<sub>2</sub>/carbonate chemistry of seawater changes. To date, very limited quantitative data exist with which to test this hypothesis, particularly in shelf environments.

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### **Data Collection and Carbonate System Research at the UNH Coastal Carbon Lab**

Since 2004 the Coastal Carbon Lab at UNH has been involved in measuring carbonate parameters in the Gulf of Maine. Our present efforts include monthly along-shore and cross-shore transects where we measure NPP, continuous pCO<sub>2</sub>, TA, nutrients, calcium, dissolved organic C & N, and a variety of physical and optical properties. In collaboration with PMEL, we also maintain a coastal CO<sub>2</sub> buoy in the western Gulf. Present research is involved in 1) Determination of the contribution of pelagic calcification to the overall dissolved inorganic budget 2) The influence of plume waters on calcite saturation state, and 3) production and disappearance of satellite derived calcite within a moving parcel of water.

**Solomon<sup>1</sup>, R.F., C.E. Ostrander<sup>1</sup>, E. Heinen De Carlo<sup>1</sup>, M.A. McManus<sup>1</sup>, F.T. Mackenzie<sup>1</sup>, K.E. Fagan<sup>2</sup>, C. Sabine<sup>2</sup> and R.A. Feely<sup>2</sup>**

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### **Coastal observing at CRIMP-CO<sub>2</sub>, Kaneohe Bay, Hawaii: A study of land-ocean interactions and CO<sub>2</sub> exchange between seawater and the atmosphere**

Human activities throughout the past two centuries have broadly changed the landscape of our environment. Changes in land use and fossil fuel burning associated with global industrialization have led to large increases in the atmospheric content of greenhouse gases and are now widely thought to cause global warming. It is also thought that climate change may increase the frequency of storms. The latter facilitate the transfer of nutrients, sediment, and pollutants from rivers into coastal ecosystems, potentially contributing to changes in how the coastal area responds to natural forcing mechanisms. There is mounting evidence that increased oceanic CO<sub>2</sub> concentrations lower the saturation state of seawater with respect to carbonate minerals, cause “ocean acidification” and, it has been argued by some, negatively impact calcification (e.g., Kleypas et al., 1999; Orr et al., 2005). Coastal areas and estuaries, however, may be either net annual sources or sinks of atmospheric CO<sub>2</sub> (-41 to 7.3 Mole C m<sup>-2</sup> yr<sup>-1</sup>, Mackenzie and Lerman, 2006), depending on local conditions.

We present here results from 18 months of observations at CRIMP-CO<sub>2</sub>, a collaborative effort in Kaneohe Bay, Hawaii between UH Manoa and NOAA/PMEL. This buoy was the first coastal buoy of the NOAA/PMEL-CO<sub>2</sub> program. CRIMP-CO<sub>2</sub> has documented the response of bay waters to pulsed inputs throughout a La Niña winter season (2005-06) and a much drier subsequent winter (2006-07). The evolution of bay waters following storm-derived inputs of freshwater, sediment and nutrients was studied, along with the impacts of blooms and physical forcing on the air-sea exchange of CO<sub>2</sub>. Although nutrient inputs typically cause phytoplankton blooms in Kaneohe Bay, physical forcing strongly influences system response, in particular stratification and mixing, hence controls both the duration of blooms and attendant changes in CO<sub>2</sub> concentration. Southern Kaneohe Bay often becomes a CO<sub>2</sub> sink following storm inputs (0.2-0.7 m Mole C m<sup>-2</sup> hr<sup>-1</sup>), but remained a net source of CO<sub>2</sub> to the atmosphere (-1.06 Mole C m<sup>-2</sup> yr<sup>-1</sup>) throughout our study period. This result is similar to estimates from Hog Reef flat in Bermuda and from

the Scheldt Estuary plume (-1.2 and -1.1 to -1.9 Mole C m<sup>-2</sup> yr<sup>-1</sup>, respectively, Mackenzie and Lerman, 2006).

**Walz, Peter M., Peter G. Brewer, Edward T. Peltzer, Rachel M. Dunk, Dale Graves, Jim Scholfield, William Kirkwood**

MBARI

**Free Ocean Carbon Dioxide Enrichment (FOCE): Control and Measurement of Ocean Seawater to Simulate a Low pH-High CO<sub>2</sub> Ocean**

Scientists and Engineers at the Monterey Bay Aquarium Research Institute (MBARI) have undertaken a series of small-scale in-situ CO<sub>2</sub> enrichment experiments in order to simulate the present and predicted future effects of fossil fuel CO<sub>2</sub> emissions on ocean pH. In excess of 25.2 gigatons CO<sub>2</sub> are added to the atmosphere each year and the ocean has been the primary sink of these emissions. Presently, the ocean is absorbing on average 1 million tons of fossil fuel CO<sub>2</sub> per 2 hours. The result of this process has been a lowering of the surface ocean pH by approximately 0.1 units during the past 100 years. Recent geochemical models project an additional drop of 0.2 units by the middle of this century.

The FOCE prototype was designed to create a controlled lowered pH condition for a freely exchanging volume of seawater 0.5 meters high by 1.0 meters diameter. A current meter and pH probes in the center of this volume provide the control feedback for driving the system to a desired pH set point (0.1 to 0.3 pH units below ambient seawater pH). The prototype system used a rotating mechanical vane and valve with eight ports, each port delivering acidified seawater to emitters that covered 1/8th the circumference of the 2-meter diameter framework. The directional valve delivered acidified seawater primarily to the upstream side of the FOCE structure. A second-generation FOCE system will use a current meter, directional resolver and electronic operation of up to 16 solenoid valves, allowing for significantly improved directional control at low flow conditions (< 10 cm/sec). For the two sea trials conducted with the FOCE prototype system, HCl was used to lower the pH of the seawater. We have now begun to envision a FOCE design that would use liquid CO<sub>2</sub> to change the local pH chemistry. A near shore cabled observatory could provide the power, communications, and a supply of piped CO<sub>2</sub> necessary for long term (weeks-months) observation and control of depressed pH levels in an ocean environment.

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**Particle settling velocities estimated using a refined “benchmark” approach average 300-400 m/d, and in most cases do not vary with depth: implications for the dissolution depth of alkalinity and the rate of ocean acidification**

Sinking particles export organic carbon to the deep ocean; they also export alkalinity in the form of calcium/magnesium carbonates, which leads to ocean acidification. The depth at which organic carbon is remineralized is important for carbon sequestration; more important for ocean acidification is the depth at which carbonate minerals dissolve.

Berelson (2002) used data from the US JGOFS NABE, EqPac, and ASPs studies to suggest that particle settling velocity (SV) tends to increase with depth, as earlier hypothesized by Honjo (1996). Berelson used a “benchmark” approach, which estimates SV's from time-of-flight of particles between pairs of traps at different depths. However, Berelson's implementation has several methodological problems, most notably an upper limit on SV's caused by the assumption of a minimum cup rotation time, and correlations between SV's estimated between upper and lower pairs of traps.

To evaluate the severity of these problems, we developed a method that improves the sensitivity of the benchmark approach. This new method, based on fitting Fourier series to time-series data, was applied to data from MedFlux, as well as from the US JGOFS NABE, EqPac, and ASPs studies. Fluxes of a



variety of tracers were plotted on linear scales, on logarithmic scales, and as molar ratios, and were fit using the new method. We estimated SV's between 26 pairs of traps, in each case making 5 estimates using different tracers. Our results showed no significant differences among SV's estimated using different tracers. There were, however, large differences between SV's estimated using single tracers and those estimated using ratios of tracers; we argue that single tracers give more reliable results. Modal settling velocities estimated using log-transformed fluxes for open-ocean sites with good temporal resolution (i.e, for sites having cup rotation times  $\leq 8.5$  d) are in the range 77-966 m/d, with average modal value 330 m/d.

These results suggest that the dissolution depth of carbonate minerals may be much deeper than predicted from slower particle sinking velocities, and therefore that the rate of return of alkalinity from depth may be much slower than predicted, increasing the rate of ocean acidification.

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**Seagrass Response to Ocean Acidification: From Individual Leaves to Populations**

Seagrasses, a polyphyletic group of aquatic angiosperms form the bases of highly productive ecosystems ranging from tropical to polar seas that support diverse assemblages of marine organisms. Despite their evolutionary and ecological success, seagrasses have high light requirements that make them vulnerable to eutrophication, sediment loading and coastal modification. Unlike most marine autotrophs, the high light requirements result from CO<sub>2</sub> limited photosynthesis because the capacity for bicarbonate utilization cannot saturate the CO<sub>2</sub> requirements of Rubisco. Despite clear evidence for carbon limitation of photosynthesis, seagrasses thrive in high light environments, and show little evidence of light-induced photoinhibition. Increasing the availability of dissolved aqueous CO<sub>2</sub> can increase instantaneous rates of light saturated photosynthesis by up to 4 fold. Prolonged exposure to elevated CO<sub>2</sub> concentrations increases the concentrations of non-structural carbohydrates (sucrose and starch), rates of vegetative shoot proliferation, and flowering, and reduces light requirements for plant survival. Consequently, seagrass populations are likely to respond positively to CO<sub>2</sub>-induced acidification of the coastal ocean, which may have significant implications for carbon dynamics in shallow water habitats and for the restoration/preservation of seagrass populations.