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First results from a controlled deep sea CO_2 perturbation experiment: Evidence for rapid equilibration of the oceanic CO_2 system at depth

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[1] We have carried out series of remotely operated vehicle–controlled oceanic CO_2 system perturbation experiments off the coast of California at depths down to 1000 m to observe reaction rates and pathways with both HCl and HCO_3^- addition. The work was done to evaluate possible barriers to carrying out future Free Ocean CO_2 Enrichment experiments to simulate the chemistry of the emerging high CO_2–lower pH ocean. A looped 460 mL flow cell with a pH sensor was used to monitor the time to equilibrium for 900 μL additions of 0.008 N HCl and for small slugs of HCO_3^-enriched seawater. The results were compared to equivalent experiments at the same temperature and 1 atm pressure. In each case the experiments at depth showed significantly faster time to equilibrium than those at 1 atm. These results are consistent with the low partial molal volume of CO_2 in seawater, favoring the hydration reaction rate. The results imply, but do not prove, a significant effect of pressure on the rate constants. The relatively rapid equilibration times observed in seawater of 4°C and at 10 MPa indicates that there are no fundamental physical chemistry limits for carrying out small-scale free-ocean CO_2 enrichment experiments.

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1. Introduction

1.1. Background

[2] It is now commonplace to carry out large-scale controlled CO_2 enrichment experiments on land to investigate the impact of increasing atmospheric CO_2 levels on terrestrial ecosystems, but no equivalent experiments have yet been carried out in the ocean. Why is that, is there a compelling need, and what are the conflicts and challenges?

[3] The extraordinary rise in fossil fuel CO_2 levels in the atmosphere has as its partner an equivalent rise in the CO_2 concentration in the ocean. The ocean has long been recognized as "a giant regulator of carbon dioxide" [*Callendar*, 1938], and with the ability to recover the oceanic fossil fuel CO_2 signal above the natural background [*Brewer*, 1978; *Gruber et al.*, 1996] scientists have been able to track the increasing oceanic CO_2 levels. About 30% of the fossil fuel CO_2 emitted to the atmosphere is quickly transferred by gas exchange to the ocean surface waters [*Intergovernmental Panel on Climate Change* (*IPCC*), 1990, 1995], and the rate of ocean uptake is now ~20–25 million t CO_2 d^{-1} (2–2.5 Gt C/yr). Without this vast present and future sink provided by the alkalinity of the ocean the world would have an extraordinary atmospheric CO_2 problem. We explicitly count upon continued oceanic uptake in all extrapolations of the future accumulation of CO_2 in the atmosphere.

[4] Yet these same projections also indicate that an unprecedented change in oceanic chemistry may occur [*Haugan and Drange*, 1996; *Brewer*, 1997; *Caldeira and Wickett*, 2003] that if taken too far may cause environmental harm [*Kleypas et al.*, 1999; *Langdon et al.*, 2000; *Riebesell et al.*, 2000]. What level is "too far," and how might we assess this? We have already reduced the pH of ocean surface waters worldwide by >0.1 pH units, and when CO_2 levels reach 600 ppm in midcentury we will have reduced the pH by 0.3. All future energy scenarios have continued fossil fuel usage, and thus a lower-pH ocean is inevitable with only the timescale at issue.

[5] On land the climatic effects of elevated CO_2 levels have been treated both as a problem – global warming, sea level rise, but also as a possible benefit in increased plant photosynthesis. It has even been suggested that the increase in terrestrial photosynthesis could greatly offset national contributions to atmospheric CO_2 levels [*Fan et al.*, 1998; *DeLucia et al.*, 1999], although this result has been strongly criticized [*Holland and Brown*, 1999; *Potter and Klooster*, 1999; *Bolin et al.*, 1999].

[6] The experimental basis for evaluating land ecosystem responses to elevated CO_2 levels has been greatly aided

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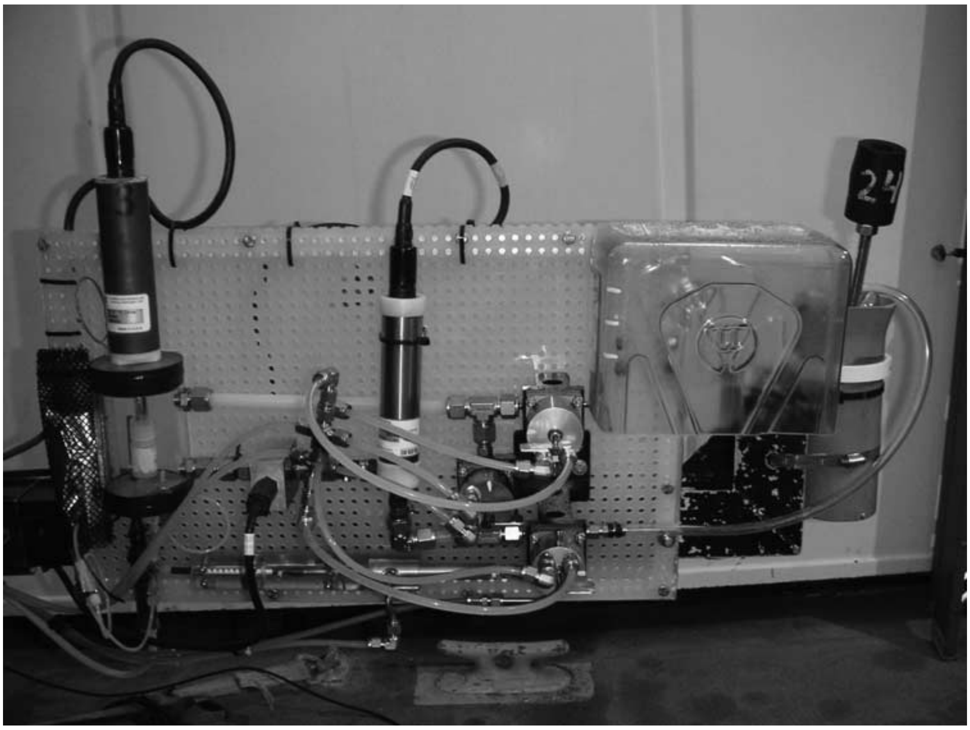

Figure 1. A photograph of the apparatus used for the field experiment. The pH electrode is seen mounted in the titration cell at far left, the circulating pump is in the center, and just to the right of this are the two hydraulically controlled valve assemblies. At far right is the inverted clear plastic container used to hold a pool of buoyant liquid CO_2, which is delivered at depth. The handle mounted in the quiver at extreme right holds the seawater intake line, which may be positioned either to draw in normal background seawater or CO_2-enriched water formed beneath the liquid CO_2 surface. The small plastic syringe used for acid injection into the pH cell is seen mounted horizontally at lower center; this too is actuated by hydraulic valve control from the remotely operated vehicle (ROV). See color version of this figure in the HTML.

by the development of Free Air CO_2 Enrichment (FACE) techniques in which a ring of controlled CO_2 diffusers release gas on the upwind side of the apparatus so that downstream sensors receive the signal and provide feedback to control the flow. In this way long-term controlled exposure of a complex, open ecosystem to a set elevated atmospheric CO_2 level is maintained. No such techniques are yet available for the equivalent oceanic experiments.

1.2. Oceanic CO_2 Experiments

[7] Large-scale aquarium experiments [*Langdon et al.*, 2000], mesocosm studies [*Riebesell et al.*, 2000; *Zondervan et al.*, 2001], and small-scale studies of the effect of elevated oceanic CO_2 levels on animal reproduction [*Shirayama*, 1997] have been carried out. Deep ocean CO_2 sequestration experiments with free release of liquid CO_2 [*Brewer et al.*, 1999, 2002; *Barry et al.*, 2003] have provided valuable information, but tidal vector forcing of the plume of CO_2-rich, low-pH water emanating from a central pool results in complex and highly variable exposure of the surrounding biogeochemical system. Carrying out the oceanic equivalent of the land based FACE experiments could alleviate this problem.

[8] There are however substantial technical barriers to doing so. With the new availability of advanced remotely operated vehicle (ROV) techniques for experimental ocean science we can visualize ways to assemble, control, and return data from, complex geochemical experiments on the ocean floor [*Kleinberg et al.*, 2003; *Brewer et al.*, 2004; *Pasteris et al.*, 2004]. However, difficult fundamental chemical challenges also arise; CO_2 released into free air is inert; only physical mixing is required to distribute the signal. Release of CO_2 into seawater initiates a complex series of reactions involving the full aqueous CO_2-H_2CO_3-HCO_3^--$CO_3^=$ system. While these species are typically treated as an equilibrium system, the slow hydration rate of the CO_2 molecule [*Johnson*, 1982; *Soli and Byrne*, 2002] can produce very significant lag times that can potentially confound an oceanic CO_2 perturbation experiment [*Zeebe et al.*, 1999; *Zeebe and Wolf-Gladrow*, 2001].

[9] The essential reaction at typical seawater pH is

$$H_2O_{(aq)} + CO_{2(aq)} \Leftrightarrow H_2CO_{3(aq)} \Leftrightarrow HCO^-_{3\,(aq)} + H^+_{(aq)},$$

where the initial nonionic reaction is slow with an Arrhenius activation energy of 74 kJ/mol [*Magid and Turbeck*, 1968].

[10] The effect of pressure on the equilibrium state of chemical species in seawater can readily be calculated with knowledge of the partial molal volumes of the reactants, and

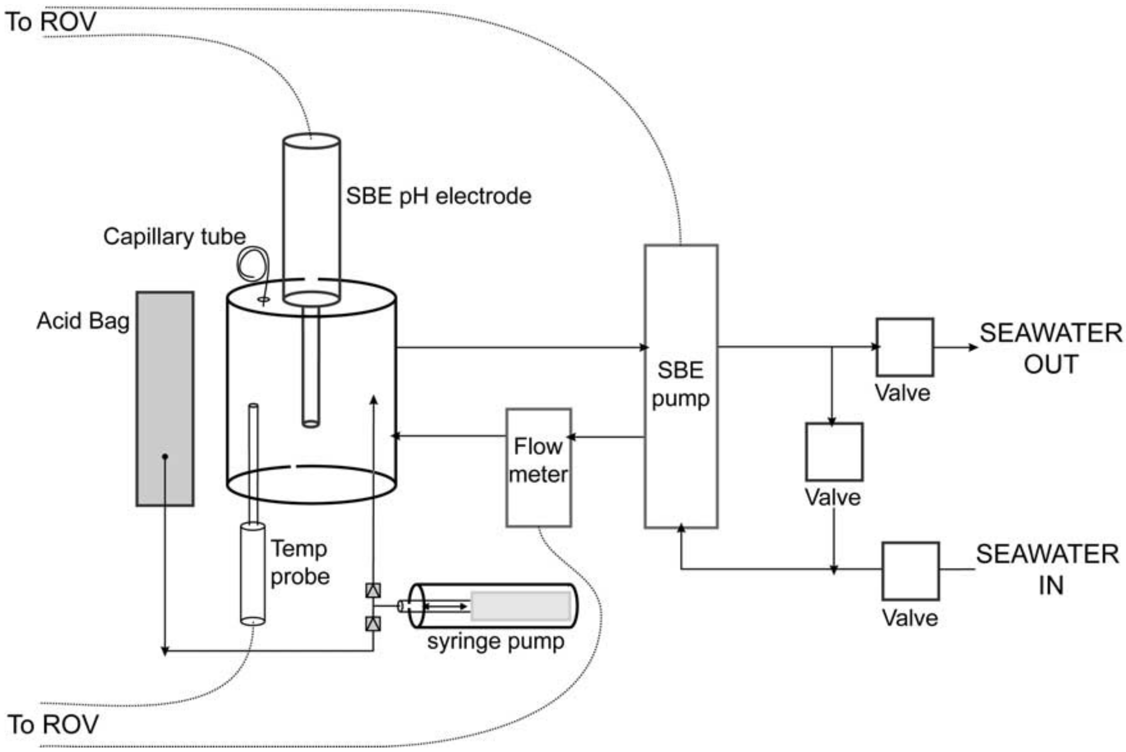

Figure 2. Line drawing of the flow scheme for the equipment shown in Figure 1, indicating the valve arrangement and injection techniques.

this is routinely done for calculating the in situ properties of the oceanic CO_2 system. However, there is no way to compute a priori the effects of pressure on the reaction rates. That must be determined experimentally.

[11] We report here an investigation of this problem, carried out through a series of small-scale time-to-equilibrium experiments at various ocean depths by injecting both hydrochloric acid, and CO_2-enriched seawater,

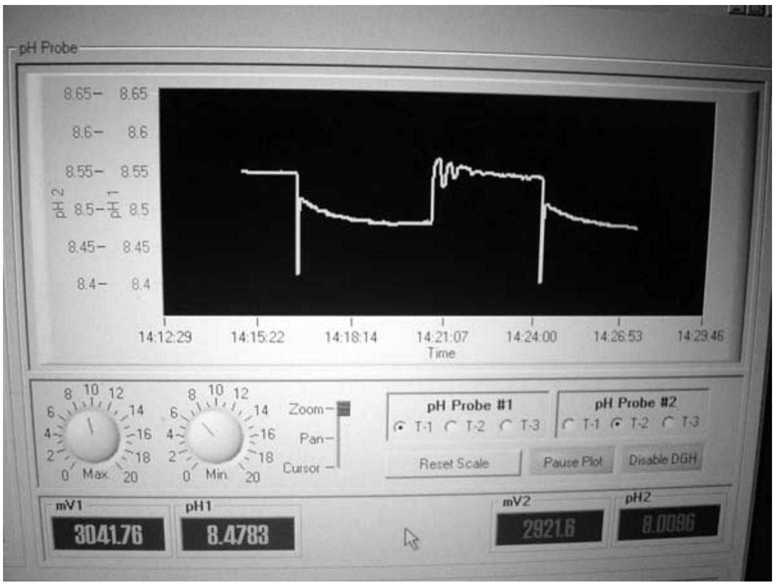

Figure 3. Screen image of the record of injection of 900 μL 0.008N HCl into the pH cell. Reading from left to right, the trace shows a stable reading of (uncorrected) pH of ~8.55, followed by a sharp drop to pH ~8.4 as the slug of HCl is inserted. The time to stabilization at the new, lower pH is assessed from analysis of the shape of the pH time curve observed. After 5 min the valves are opened several times, and the system is flushed. The oscillating pH signal results from venting of low-pH water trapped in the dead space between the inlet and outlet valves. A second experiment is then initiated, and the sequence is repeated. See color version of this figure in the HTML.

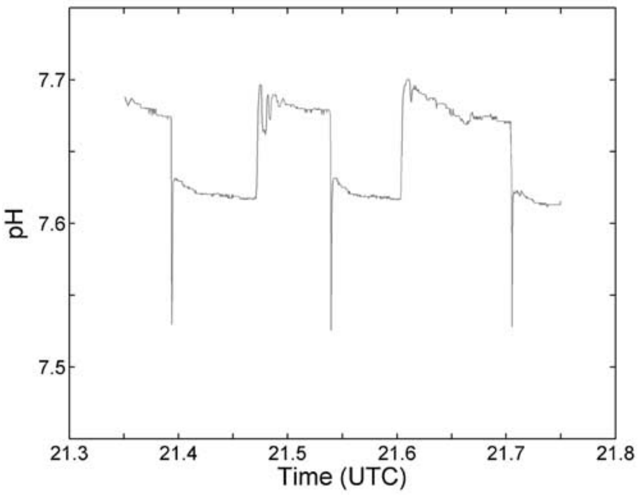

Figure 4. The data record of pH changes from a series of three injections of acid at a depth of 500 m. The pH electrode output is sampled at 2 Hz. Mixing in the cell accounts for the initial rapid ΔpH, and the chemical system then relaxes toward equilibrium with a time constant defined by the shape of the pH time curve, which here trends to lower pH with time. This is consistent with formation of an intense cloud of CO_2 at the point of injection, followed by hydration of the excess CO_2 to form HCO_3^-. See color version of this figure in the HTML.

into a looped flow cell and observing the response time at depth.

2. Methods

2.1. Apparatus

[12] The experiments created here are simple in concept, but difficult to execute. We constructed a flow loop system (Figures 1 and 2) that permitted seawater at a selected depth to be drawn in to the unit, and circulated through a flow cell equipped with a pH electrode (Seabird Elecronics, Inc., SBE 18) and a thermistor for logging temperature. The internal volume of the cell and associated valves and tubing was approximately 460 mL. Hydraulic valves, actuated under ROV control, were used to open and close the inlet and outlet ports. Data logging was by laptop computer in the vehicle control room, using MBARI created software. A screen image of the data acquisition system is shown in Figure 3.

[13] For the acid injection experiments a 1 mL syringe permitted injection of 900 μL of 0.008 N HCl in 0.5 M NaCl into the cell at each stroke, much as in a classic alkalinity titration [*Bradshaw et al.*, 1981]. A small capillary loop, open to the ocean, served to accommodate the volume increase.

[14] For the CO_2-enriched water injections an inverted box, crafted from cutting a laboratory polyacrylic carboy, was attached to the frame to contain approximately 1 L liquid CO_2 delivered at depth following techniques described earlier [*Brewer et al.*, 1999]. Seawater trapped in close contact with the liquid was strongly enriched in dissolved inorganic carbon (DIC), primarily in the form of HCO_3^- ion, and a slug of this water could be drawn into the cell by using the vehicle robotic arm to place a wand, with inlet tube attached, in the pool of CO_2-rich water. The hydraulic valves were then rapidly opened and closed with the recirculating pump running, so that a small slug (of indeterminate volume) was introduced into the circulating flow.

2.2. Field Work

[15] The experiments described here took place on 27 and 28 January 2004 in Monterey Bay, California, using the RV Point Lobos, and the ROV Ventana as experimental platforms for equipment deployment and control. Bad weather on 27 January curtailed activities, and work on that day served mainly as a test to assure that the system would yield reliable data, and to make small adjustments to the point of delivery of the acid so that the low-pH water at the capillary tip passed once through the circulation loop to become well mixed before contacting the pH electrode surface.

[16] The procedure followed on 28 January 2004 was to dive the vehicle to 1000 m depth, and carry out a set of three acid injections, followed by a series of three injections of highly CO_2 enriched water. Both single strokes of the syringe, and double strokes, were used so as to examine the relaxation times at differing ΔpH. The cell configuration remained the same for all dives, and each experiment was allowed to run for 5 min. The vehicle was then brought to

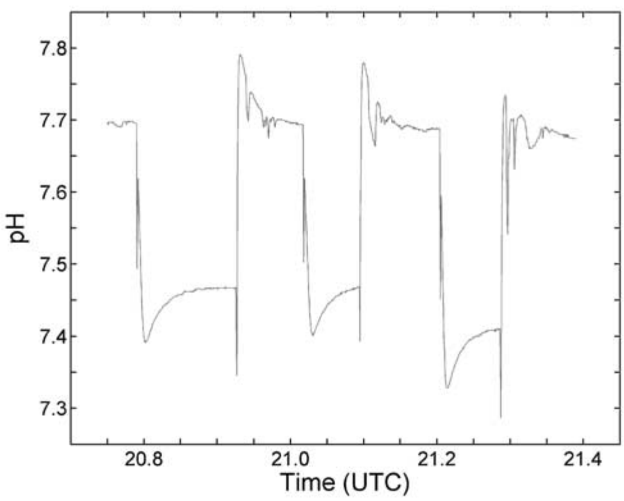

Figure 5. Equivalent data plot as for Figure 4, but in this case a slug of seawater, highly enriched in HCO_3^- by dissolution from a liquid CO_2 interface, is drawn into the cell and recirculated. The trend with time is to higher pH as the system adjusts to equilibrium. Both the forward and back reactions are proceeding simultaneously; the net result of a rapid decrease from injection of low-pH water, followed by a slower increase in pH as the system equilibrates, is consistent with removal of an excess of HCO_3^- over the equilibrium value. See color version of this figure in the HTML.

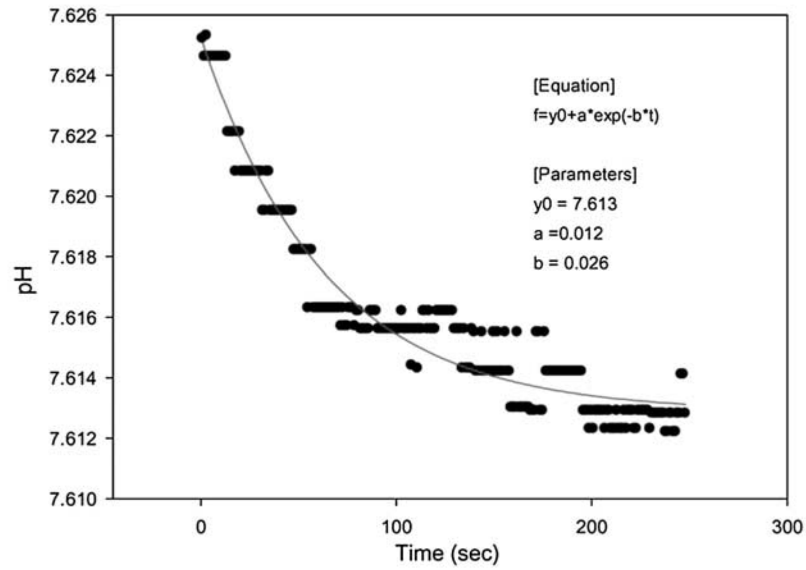

Figure 6. Plot of pH versus time for an acid addition experiment at 500 m depth, with the derived coefficients shown. The modeled data are those obtained after the initial sharp drop and rebound in pH, seen in Figure 4 as the segment where the exponential decline to a steady value occurs. See color version of this figure in the HTML.

shallower depth, and the exercise repeated at 500 m, and at 100 m depth.

3. Results

[17] The raw sensor (electrode + preamplifier) output voltage obtained was first converted to pH by using the equation

$$pH = 7 + (V_{out} - \text{offset})/(K \times T \times \text{slope}),$$

where V_{out} is the pH electrode output voltage, $K = (R/F) \times \ln 10 = 1.98416 \times 10^{-4}\ V\ K^{-1}$, R is the gas constant (8.31434 K^{-1} mol^{-1}), F is the Faraday constant (9.6486 $\times$ 10^4 C mol^{-1}), and T is temperature in Kelvin. In the following discussion, all times are given in UTC as recorded by the ship/ROV experimental system.

[18] The first experiment at 1000 m depth, $T = \sim 4°C$, $S = 34.517$, was initiated at 1802 UT with injection of single 900 μL stroke of HCl. These single stroke acid injections were carried out three times, and then a double stroke was

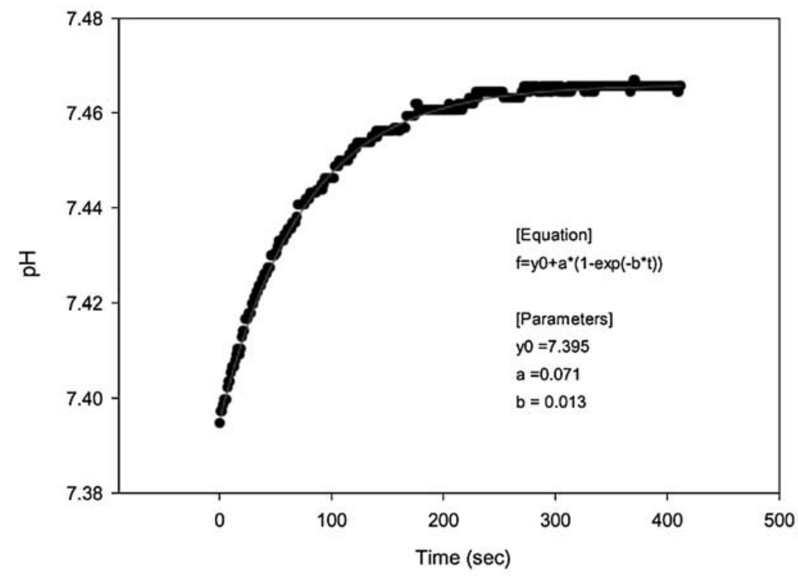

Figure 7. The result of analysis of the relaxation time from addition of a slug of CO_2-rich water at 500 m depth. Note the different trend to the acid addition experiment shown in Figure 6. See color version of this figure in the HTML.

Table 1a. Calculated Half-Life of the Relaxation Time in pH: Laboratory Measurements of the Relaxation Time With HCl Injection at 1 atm

Temperature, °C	Relaxation Half-Life, s
4.2	187
9.0	100
11.7	87
13.8	69

also done three times under same conditions. Our on−site review of the data revealed small inconsistencies in equilibration times, and this was traced to inadequate flushing of the dead space between the valves between experiments. Experimental procedure was therefore altered to adjust for this at other depths (Figure 4).

[19] Injection of CO_2-enriched water at 1000 m depth was initiated at 1919 UT, after the HCl injection experiments were complete, and repeated four times. These indicate that the sharp peak of pH at the time of injection of CO_2-enriched water is associated with the opening and closing of the hydraulic valve operation. We observed a system decrease about 0.2 pH units immediately, followed by relaxation to a new equilibrium condition; the kinetics of this process includes both chemical equilibration and water mixing. We continued similar HCl injection and CO_2-enriched seawater injection experiments at 500 m depth, $T = \sim 6°C$, $S = 34.301$, and 100 m depth, $T = \sim 10°C$, $S = 33.683$. The plots of pH versus time at 500 m depth are shown in Figures 4 and 5 for a series of HCl injection, and CO_2-enriched seawater injection, runs respectively.

[20] The relaxation to equilibrium was approached from different directions in these series once the initial large drop in pH occurred. Although both injection series result in lowered pH they differ in important details. For acid injection we change pH and alkalinity, but not the mass of CO_2. For the CO_2-enriched water addition we do not change alkalinity. For the acid addition the volume added is small and tightly specified. For the CO_2 enrichments the volume is larger, and not precisely known.

[21] Both the forward and back reactions are proceeding simultaneously in each scheme. For the acid injection the system first overshoots, then trends to lower pH with time. This is consistent with formation of an intense cloud of CO_2 at the point of injection, followed by slower hydration of the excess of CO_2 molecules over the equilibrium value to form the equilibrium quantity of HCO_3^-.

[22] For the HCO_3^--enriched seawater injections the net result is a rapid decrease from injection of low-pH water, followed by a slower increase in pH as the system equilibrates. This is consistent with removal of a temporary excess of HCO_3^- over the equilibrium value.

Table 1b. Calculated Half-Life of the Relaxation Time in pH: In Situ Field Measurements of the Relaxation Time at Depth by Both Acid and CO_2-Enriched Seawater Injection

Temperature, °C	Depth, m	Mean Relaxation Half-Life, s	Technique
10	100	57 (n = 3)	HCl injection
6	500	29 (n = 3)	HCl injection
6	500	49 (n = 3)	CO_2-rich seawater injection
4	1000	46 (n = 4)	CO_2-rich seawater injection

Table 2a. Coefficients of the Equation Used to Determine the Relaxation Time in pH: Laboratory Data at 1 atm From HCl Injection[a]

Fitting Curve Equation	Parameters		
	y_0	a	b
$f = y_0 + a^*(1 - \exp(-b^*t))$	8.2418	0.1705	0.0037
	8.0679	0.1886	0.0069
	8.0869	0.1745	0.0080
	8.0873	0.1934	0.0100

[a]In each case the results were treated as an exponential decay function designated as $f = y_0 + a^*(1 - \exp(-b^*t))$, where b is the decay constant in s^{-1}.

[23] We have fit the data obtained to an exponential relationship. For the HCl injection experiments, the relaxation time (f) of a perturbation in pH is given by

$$f = y_0 + a^*(\exp(-b^*t)).$$

For the CO_2-enriched seawater experiments we use the function

$$f = y_0 + a^*(1 - \exp(-b^*t)),$$

where in both cases t is the time in seconds, and y_0, a, b are the determined coefficients.

[24] The results of this analysis are shown in Figures 6 and 7 where representative equilibration curves in pH with time for an experiment at 500 m depth are shown. In each case the relaxation time to a new equilibrium value was far shorter than that experienced in laboratory studies at 1 atm at the same temperature. The results of the half-lives obtained from these in situ experiments, together with results from laboratory studies for comparison, are shown in Tables 1a and 1b. The coefficients derived are shown in Tables 2a and 2b.

[25] In each case the time to equilibrium observed was faster for the acid injection experiments than for the introduction of HCO_3^--enriched seawater (Tables 1a and 1b). We hypothesize that this is due to the relative volume changes as equilibrium is approached. For an excess of free CO_2 molecules converting to HCO_3^- the ΔV is negative, and thus higher pressure favors the reaction. For an excess of HCO_3^- the sign is reversed, and equilibrium is reached more slowly. Both these effects are small compared to the overall increase in rates observed.

[26] While the exact numerical values derived here are somewhat apparatus-dependent in that they include a mixing term there is one clear trend. In similar laboratory experiments of HCl injection to surface seawater at 1 atm (Tables 2a and 2b), the trend of the relaxation times observed, as is widely known, is to become slower with decreasing temperature. In the in situ experiments in each case the relaxation time was faster at lower temperature. These experiments suggest that the high pressures in the deep sea have a strong impact on the equilibration time, overcoming the effect of lower temperature.

4. Discussion

[27] The problems of very long times to equilibrium for the classic TCO_2-alkalinity acid titration of seawater

Table 2b. Coefficients of the Equation Used to Determine the Relaxation Time in pH: Coefficients Determined From Field Experiments at Depth From Injection of Both HCl- and CO_2-Enriched Seawater

Depth, m	Fitting Curve Equation	Parameters			Memo
		y_0	a	b	
100	$f = y_0 + a^*(\exp(-b^*t))$	8.201	0.035	0.013	HCl injection
500		7.616	0.011	0.028	HCl injection
500		7.377	0.071	0.014	CO_2-enriched seawater injection
1000		7.255	0.063	0.016	CO_2-enriched seawater injection

[*Dyrssen and Sillen*, 1967; *Bradshaw et al.*, 1981] for small perturbations near the initial pH are familiar to most ocean chemists. It is in large part for this reason that most laboratory titrations are run at 25°C. At low temperatures the timescales are frustratingly long and thus the determination of the apparent stability constants of the CO_2 system in seawater at low temperature is notoriously difficult. Thus it was with some surprise that we first observed the extraordinarily speed with which equilibrium was reached at 4°C, but at 10 MPa pressure.

[28] Surprisingly, the reaction pathway for this system is not well known. *Johnson* [1982] used transition state theory, in which the reactants are in equilibrium with an activated complex that dissociates to form the products, to correct his results on the rate constants for seawater, but did not specify the complex. The reaction involves breaking of one of the CO_2 double bonds and is also accompanied by a bending of the CO_2 molecule. The reaction is approximately athermic.

[29] An answer was provided by *Jonsson et al.* [1977, 1978], who carried out ab initio molecular orbital calculations of the reaction $H_2O + CO_2 \rightarrow H_2CO_3$, and the reaction $OH^- + CO_2 \rightarrow HCO_3^-$, and identified a possible transition state (Figure 8). They found no barrier to reaction in the gaseous state, and suggested that the slow reaction in solution must therefore be associated with solvation effects. Specifically they suggested that the transition state identified from the reaction with OH^- in the gas phase should also be valid for the reaction $H_2O_{(aq)} + CO_{2(aq)} \leftrightarrow H_2CO_{3(aq)}$. We therefore hypothesize that the increase in reaction rate with pressure is associated with changes in the solvation sphere surrounding the dangling proton in the model of *Jonsson et al.* [1978].

[30] The exact value of the enhancement in rate due to pressure effects cannot be measured accurately here. The apparatus we have used is designed for in situ work, and cannot be easily adapted to laboratory studies. The precise response time of the system is dependent on experimental variables and is a diagnostic, not a fundamental, number.

[31] However we can make some approximations. In a classic alkalinity titration the sequence of events may be described as follows. At the acid injection tip a cloud of low-pH water is created which, due to the rapid dehydration step, creates a cloud of free CO_2 molecules. These are mixed into the bulk fluid and a complex set of acid-base reactions occurs [*Bradshaw et al.*, 1981; *Zeebe and Wolf-Gladrow*, 2001]. The free CO_2 molecules are not recorded by the pH electrode, thus accounting in part for the rebound of the curves shown in Figure 4. The slow hydration reaction of CO_2 then is the rate-limiting step, and as hydration occurs $CO_3^=$ ions are consumed and the pH slowly drops. It is this part of the reaction curve that we model as an exponential decay. If (we stress the conditional) we can take this function as an approximation to the actual hydration rate, then we can compare the decay constants (Tables 2a and 2b) to known values [*Johnson*, 1982; *Soli and Byrne*, 2002]. In our 500 m depth experiment (5.9°C) we obtain a decay constant of 0.028 s^{-1}. The 1 atm result of *Johnson* [1982] indicates a value of 0.0046 s^{-1} at this temperature. Thus the effect we observe appears to be an enhancement of the hydration reaction rate by about a factor of 6 at our 500 m depth and at 5.9°C. This is consistent with our 1 atm decay times reported in Tables 2a and 2b. The result reported by *Brewer et al.* [2005] for a preliminary experiment carried out a 3960 m depth (1.6°C) indicates far greater rate enhancements at higher pressures.

[32] In fieldwork at a single site we cannot vary pressure and temperature independently. Nonetheless the rapidity of the observed time to equilibrium at depth provides convincing evidence of the feasibility of carrying out controlled deep ocean CO_2 perturbation experiments that may help uncover the emerging effects of steadily increasing ocean acidification on marine biogeochemical and ecological

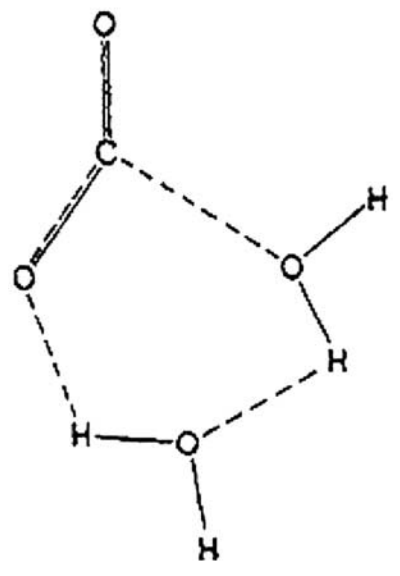

Figure 8. From *Jonsson et al.* [1977]. Their Figure 5 shows the transition state proposed for the reaction of CO_2 with H_2O. Their model calculations showed an unusually long C-OH distance of 1.43 Å. Since there are no barriers to reaction in the gas phase solvation effects, they suggest that effects associated with the hydration sphere of the dangling proton provide a plausible explanation of the slow hydration rate observed at 1 atm. Thus the effect of pressure on this hydration sheath also offers a plausible explanation for the higher reaction rates we report here.

systems. The surprising increase in reaction rate we have uncovered may have significance for the respiration of marine animals at depth.

[33] **Acknowledgments.** This work would not have been possible without the efforts of the captain and crew of the R/V *Point Lobos* and the skilled work of the pilots of the ROV Ventana. The manuscript benefited from the careful work of two anonymous reviewers. D. Wolf-Gladrow has pointed out that the strong correlation of carbonate ion decrease with depth may also account for a chemical kinetic enhancement of rates. We acknowledge the support of the David and Lucile Packard Foundation to MBARI. The participation of Noriko Nakayama was made possible by a Research Fellowship from the Japan Society for the Promotion of Science. Support was provided by an International Research Grant from the New Energy and Industrial Technology Organization (NEDO) and the U.S. Dept. of Energy Ocean Carbon Sequestration Program (grants DE-FC26-00NT40929 and DE-FC03-01ER6305).

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