Feasibility of Large-Scale Ocean CO₂ Sequestration

Annual Report

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ABSTRACT:

The project accomplishments in 2005 have been exceptional, and have seen radical new techniques successfully devised and implemented. At the outset the goal set was to create a system dubbed FOCE – Free Ocean CO₂ Enrichment – for investigating the impact of rapidly growing ocean CO₂ levels from passive absorption by the surface ocean. A paper describing progress in this area is included with this report. On June 29, 2005 the P.I. presented a seminar on this work at NETL, and after discussion with Program Officers it was suggested that a return to the original project focus of investigating direct disposal techniques, rather than passive disposal effects, should be undertaken.

This suggestion was rapidly acted upon, and in November 2005 a major field breakthrough was accomplished in collaboration with colleagues from NETL, MIT, and AIST (Japan). In this effort the real time three-dimensional acoustic detection of a freely released small-scale CO₂ plume was accomplished. In addition we have successfully field tested the theoretical model of Zeebe and Wolf-Gladrow for CO₂ system kinetics at depth, thus leading to more accurate prediction of the local pH perturbations of a CO₂ plume.

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INTRODUCTION:

This year has seen excellent progress in construction and testing of a new experimental array, FOCE – the Free Ocean CO₂ Experiment, systems both in the test tank and in field testing. A report prepared for a major engineering/science conference on the science enabled by the new generation of cabled sea floor systems is attached.

The development of in situ laser Raman techniques, pioneered as novel technology under this award, has been completed, and major papers are listed in the appendix. The second generation system has proved exceptionally robust, and has been used at sea to explore the real time dissolution of liquid CO₂ source into sea water depth.

With colleagues from Japan and Norway we have published the results of a difficult 4,000m deep CO₂ injection experiment designed to examine sensing of the plume emanating from a deep-sea CO₂ source.

EXECUTIVE SUMMARY:

We provide here documentation of progress in three critical areas relating to testing concepts of deep-ocean CO₂ disposal.

i) Free Ocean CO₂ Enrichment (FOCE)

Free air CO₂ enrichment experiments (FACE) are commonplace on land, and a large international network of experimental sites now exists. DoE takes credit for being the originator of such powerful and widely used technologies. But no ocean equivalent exists, in spite of the very large fossil fuel CO₂ changes taking place there – the ocean CO₂ invasion rate is now approximately 1 million tons per hour. We have designed and field tested a prototype system for carrying out such experiments (Fig. 1)

Figure 1. The FOCE prototype system in the MBARI test tank. Opening and closing of the central valve assembly is guided by the vane. Acid flow is thus directed to the ring of soaker hose emitters, and feed-back is provided by a ring of pH sensors.

The prototype system uses acid release to control pH. A second generation system will use CO₂ enriched sea water.

ii) Sea Water CO₂ Enrichment Technique

We have designed, tested, and published, a procedure for producing highly CO₂ enriched sea water at depth. The system uses a CO₂-sea water contact chamber, and a sensing chamber where full system equilibration is reached. Sensing was accomplished by pH measurement, and by real time Raman spectroscopy to identify the individual species present.

iii) In a very small scale pilot experiment carried out in late 2004 we discovered the extraordinarily strong acoustic response at 675 kHz of a small cloud of liquid CO₂ droplets. The response is due both to the high sound velocity contrast with sea water, but also in part due to resonance effects associated with the hydrate shell. We have used this to detect both by ROV carried scanning sonar, and ship board (38 kHz) echo sounder, the signal of a plume of only 5 liters of liquid CO₂ released at 1000m depth. The plume was tracked

for 30 minutes and over 150m of ascent (Fig. 2). The result offers a powerful way to test theoretical models, and provides a mechanism for the study of biological impacts.

Figure 2. The ship board (38 kHz) acoustic detection of release of 5 L liquid CO₂. The horizontal time scale is in minutes; the vertical scale lines are 50m. Initial release was just below 1000m. The pink stepped lines show the acoustic signal of the ROV itself as it followed the rising plume.

EXPERIMENTAL:

The experimental techniques we have devised are numerous, and cannot easily be broken out in a separate section. They are described in detail in the papers in the Appendices to this report.

RESULTS AND DISCUSSION:

Each of the papers presented here contains a “Results and Discussions” section. All are directly related to the theme of both active and passive ocean CO₂ disposal, the techniques, knowledge, and environmental consequences.

CONCLUSION:

Each of the papers attached here contains the conclusions reached from the work reported.

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Presentations and Invited Lectures

January 17, 2005. AGU Chapman Conference on Carbon Sequestration, San Diego. Invited speaker.

March 7 – 11, 2005. Invited speaker: German Physical Society “Einstein Jahr” , Berlin. “Experiments on the ocean disposal of fossil fuel CO₂”; “Advances in chemical physics in the deep ocean: NMR and Raman Spectroscopy at 3.5 km depth.”

March 24, 2005. Invited speaker: Colorado School of Mines. Hydrates Symposium.

April 11, 2005. Hopkins Marine Station, Stanford University. “The ocean in a high CO₂ ”

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White, S.N., P.G. Brewer, E.T. Peltzer (2005) Determination of gas bubble fractionation rates in the deep ocean by laser Raman spectroscopy. *Mar. Chem.* In Press.

Annual Report – DoE STI
Period: 10/01/2004 – 9/30/2005

This reporting period 10/01/2004 to 9/30/2005 has been exceptionally busy and productive. We report several major publications and presentations at both national and international meetings.

Presentations and Invited Lectures

January 17, 2005. AGU Chapman Conference on Carbon Sequestration, San Diego.
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Project Report

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At the close of the project period advanced plans had been made to execute a significant new experiment to test the remote acoustic detection of a freely rising CO₂ plume. The work is scheduled for November 2005, and is to be carried out in collaboration with Dr. Robert Warzinski (DoE, NETL), Prof. Arthur Baggeroer (MIT), and Dr. Baixin Chen (AIST, Japan).

Deep ocean experiments with fossil fuel carbon dioxide: Creation and sensing of a controlled plume at 4 km depth

by Peter G. Brewer¹, Edward T. Peltzer¹, Peter Walz¹, Izuo Aya², Kenji Yamane²,
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ABSTRACT

The rapidly rising levels of atmospheric and oceanic CO₂ from the burning of fossil fuels has lead to well-established international concerns over dangerous anthropogenic interference with climate. Disposal of captured fossil fuel CO₂ either underground, or in the deep ocean, has been suggested as one means of ameliorating this problem. While the basic thermodynamic properties of both CO₂ and seawater are well known, the problem of interaction of the two fluids in motion to create a plume of high CO₂/low pH seawater has been modeled, but not tested. We describe here a novel experiment designed to initiate study of this problem. We constructed a small flume, which was deployed on the sea floor at 4 km depth by a remotely operated vehicle, and filled with liquid CO₂. Seawater flow was forced across the surface by means of a controllable thruster. Obtaining quantitative data on the plume created proved to be challenging. We observed and sensed the interface and boundary layers, the formation of a solid hydrate, and the low pH/high CO₂ plume created, with both pH and conductivity sensors placed downstream. Local disequilibrium in the CO₂ system components was observed due to the finite hydration reaction rate, so that the pH sensors closest to the source only detected a fraction of the CO₂ emitted. The free CO₂ molecules were detected through the decrease in conductivity observed, and the disequilibrium was confirmed through trapping a sample in a flow cell and observing an unusually rapid drop in pH to an equilibrium value.

1. Introduction

a. Background

The extraordinary rise in fossil fuel CO₂ concentrations in both the atmosphere (IPCC, 1990, 1995) and the oceans (Brewer, 1978; Sabine *et al.*, 2002) and the associated problem of climate change, has lead to debate over possible solutions. Some 30% of the CO₂ disposed of in the atmosphere is rapidly transferred to the ocean through gas exchange, and in the very long term the ocean will take up some 85% of all fossil fuel emissions. It was

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this that led Marchetti (1977) to suggest direct deep ocean injection of CO_2 as a possible solution to the climate problem. This theme has been revisited many times, notably by the U.S. President's Council of Advisors on Science and Technology (PCAST, 1997) who issued a report recommending storage of CO_2 as a hydrate on the ocean floor. The PCAST report indicated a belief that since the temperature and pressure conditions in the deep ocean favor formation of a solid CO_2 hydrate ($\text{CO}_2 \cdot 6\text{H}_2\text{O}$), the solid once formed would be thermodynamically stable.

There have now been many analyses of the behavior of CO_2 within the oceanic hydrate-forming regime and the complexity this introduces (Haugan and Drange, 1992; Cole *et al.*, 1993; Stegen *et al.*, 1993; Morishita *et al.*, 1993; Shindo *et al.*, 1993; Handa and Ohsumi, 1995). Small-scale laboratory experiments have been carried out in Japan (Aya *et al.*, 1992; Kimuro *et al.*, 1993; Ohgaki *et al.*, 1993; Ozaki *et al.*, 1993; Saito *et al.*, 1995; Kobayashi *et al.*, 1995), and in the US (Masutani *et al.*, 1993) to investigate this problem. Nakashiki *et al.* (1991) conducted the first field experiment using solid CO_2 (dry ice) and measured its descending velocity. Aya *et al.* (1993) made laboratory measurements of the dissolution rate of a static hydrate-coated CO_2 droplet. Brewer *et al.* (2002) made field measurements of the shrinking rate of a rising stream of hydrate-coated CO_2 droplets released at 800 m depth off the coast of California.

Brewer *et al.* (1998, 1999) investigated the formation of a CO_2 hydrate through a series of *in situ* experiments, and Rehder *et al.* (2004) have shown that true "storage" as a hydrate is not possible. The essential condition for hydrate stability is the equality of chemical potential in all three phases (water, solid, and hydrate guest molecule). Since normal seawater is very much undersaturated with respect to CO_2 , the hydrate exposed to deep waters will soon dissolve. The boundary condition is set by the formation of a diffusive CO_2 saturated boundary layer, and the rate of dissolution is governed by the thickness of this layer (Santschi *et al.*, 1991), and is in proportion to the square root of local water velocities (Hirai *et al.*, 1995). Aya *et al.* (1991, 1993, 1995) measured this dissolution rate by a high-pressure loop. The balance of the formation and dissolution rates of hydrate determines the thickness of the hydrate skin.

The study of the dissolution of a mass of liquid CO_2 placed on the ocean floor is therefore not an easy problem, although laboratory experiments provide some guidance (Aya *et al.*, 1995; Fujioka *et al.*, 1995; Masutani *et al.*, 1995; Nishikawa *et al.*, 1995; Shindo *et al.*, 1995; Uchida and Kawabata, 1995). The first experimental challenge is to safely contain and precisely deliver the material to the deep ocean. Brewer *et al.* (1999) reported development of an accumulator system, carried by an ROV, which permits active experimental control to compensate for the large volume changes undergone by the highly compressible liquid CO_2 during descent to the sea floor. This approach has been used in modified form (Peltzer *et al.*, 2003; Brewer *et al.*, 2003) to accommodate larger volumes ever since.

Specific Gravity of Liquid CO₂ in Deep Sea

Figure 1. General illustration of the specific gravity of liquid CO₂ compared to ocean water properties. The high compressibility of the liquid, and the narrow distribution of temperature in the deep sea, results in gravitational stability of a CO₂ pool at depths >3000 m.

b. Characteristics of liquid CO₂ and the reaction with seawater

The physical behavior of CO₂ under oceanic conditions is well known. At shallow depths CO₂ is in the gas phase, and it condenses to the liquid state at depths of ~400 m depending upon the local temperature regime. In typical ocean waters, CO₂ will form a solid hydrate at depths as shallow as 350 m; in a warm water basin such as the Mediterranean or Red Sea, the thermal forces will always exceed the hydrate van der Waals forces, and no hydrate will form. Whether hydrate forms or not, the boundary condition on the seawater side of the interface is set by the solubility of CO₂ at the local pressure and temperature. Liquid CO₂ is highly compressible; seawater is highly incompressible (Fig. 1). The net result is that a density reversal occurs so that CO₂ is buoyant above about 2700 m depth, is neutrally buoyant at about 2800 m depth, and forms a sinking plume below about 3000 m depth, with the approximations due to locally varying oceanic T and P.

Once CO₂ is dissolved in seawater, a complex series of processes occurs. The first step is slow hydration (Johnson, 1982; Soli and Byrne, 2002) of the CO₂ molecule to form H₂CO₃, followed by rapid ionic exchanges to form the well-known HCO₃⁻–CO₃²⁻ equilibria established at the local pH. Yet so slow is the hydration-dehydration step measured at 1 atmosphere that at temperatures of 1–2 degrees it may take tens of minutes for equilibrium

to be established, so that in a field experiment local advection may remove the reactants far from the observing site before equilibrium is reached. The effect of pressure on the reaction rates is unknown.

The solubility of CO_2 in seawater at low temperatures and at high pressure (Aya *et al.*, 1997), is far greater than for a normal atmospheric gas (Wiebe *et al.*, 1933) and the low partial molal volume of CO_2 ($31 \text{ cm}^3/\text{mol}$) relative to its molecular weight (44) ensures that CO_2 enriched seawater, at equilibrium, has significantly greater density (Haugan and Drange, 1992). Thus the plume emanating from a local CO_2 source has a complex chemical signature, is possibly not at equilibrium, and may be sufficiently increased in density that plume dynamics are affected.

The surface of the liquid source for the plume is itself complex. The boundary between the liquid CO_2 and seawater is characterized by the existence of a hydrate skin with unusual properties (Yamane *et al.*, 2000). The surface readily deforms but is not elastic in the normal sense—for relatively slow stretching rates the rate of hydrate re-building renews the surface skin so that continuity is preserved. For faster stretching the hydrate nucleation kinetics are overcome and a simple liquid CO_2 –seawater interface is presented. Although the density of the solid CO_2 hydrate is greater than that of either seawater or liquid CO_2 at depths above 5 km, a thin film may not be expected to sink to the bottom of the fluid because the mechanical strength of the film is much larger than the small gravitational force due to the density difference between CO_2 hydrate and CO_2 -saturated seawater (Yamane *et al.*, 2000). Only when active convection is induced, either by external mechanical force, such as the shaking normally used in laboratory studies, or by self-induced flow (Brewer *et al.*, 1999) can large-scale solid hydrate formation occur.

c. Experimental plan

If deep-ocean CO_2 sequestration is to be considered, then the phenomena described above are the essential features for study. A gravitationally stable pool of CO_2 on the sea floor can only be created at depths below 3000 m; however the density difference between CO_2 and seawater at this depth is still very small, and the entire experimental pool could very easily be destabilized. For this reason we selected 4000 m depth for the experiment reported here. This possibly sets a depth record for this class of work, and the increased $\Delta\rho$ permits more robust examination of the effects of physical forcing of the interface to create an experimental plume.

The principal concerns over any proposed sequestration strategy are safety, the containment lifetime, and biological impacts. It is the latter that has drawn most attention (Auerbach *et al.*, 1997; Tamburri *et al.*, 2000; Seibel and Walsh, 2001), and the fate of organisms exposed to a plume of low pH-high CO_2 water must be investigated. Yet even if no direct injection of fossil fuel CO_2 takes place, we are faced with the inevitable prospect of a significantly lower pH ocean (Haugan and Drange, 1996; Brewer, 1997) from the already massive surface invasion of the fossil fuel transient. If we are to evaluate the impacts these high CO_2 levels will cause (Cicerone *et al.*, 2004) then we must consider

controlled experiments in which we artificially elevate the CO₂ levels of the local ocean environment in much the same way that ecosystems on land are exposed to higher atmospheric CO₂ levels (DeLucia *et al.*, 1999; Shaw *et al.*, 2002). Lessons learned here may guide us.

In preparatory work (Brewer *et al.*, 2004) we have investigated the turbulent signature of the pH of a very small-scale plume emitted from the surface of a pool of CO₂ trapped (in an inverted experimental box) at 650 depth. This served to develop the deployment technique and to set the time and space scales required for sensing of the CO₂ plume. It also led to the observation of strikingly large fluctuations in pH close to the CO₂ source, far larger than might be expected from turbulence alone, leading us to speculate that parcels of water with rapidly changing degrees of equilibrium might be passing by the sensor. Here we test this hypothesis further.

In this paper we describe the controlled formation of a plume of CO₂ rich water at great depth by forcing seawater flow over the liquid CO₂ surface. We present the results from sensing of this plume by both pH and conductivity sensors. In a companion paper, Hove and Haugan (2005) analyze the fluid dynamics of the liquid CO₂ surface.

2. Materials and methods

a. 56L CO₂ accumulator

For this experiment the 56L CO₂ accumulator (Peltzer *et al.*, 2004) was thoroughly re-built. A new carbon fiber reinforced fiberglass barrel was fabricated and the aluminum end-caps and piston were replaced with ones made from titanium to alleviate problems with corrosion. The end-caps and piston were redesigned to eliminate voids on the seawater side, while increasing the depth of the recessed cavity on the CO₂ side to allow for an internal cooling loop. The extended length of the CO₂ end-cap also allowed for a second O-ring seal to solve the leakage problems encountered earlier.

b. Benthic flume

In order to have more operator control over the plume created during the release experiments, a ‘benthic flume’ was constructed (Fig. 2). It consisted of a trough for CO₂ 150 cm long, 40 cm wide and 25 cm deep; a thruster (driven by a computer controlled brushless DC motor) to generate a variable seawater current along the CO₂ trough; and a wave generator paddle. Both the wave paddle and the thruster were controllable in finite increments by the experimentalist in real-time. A clear panel on the front, and an opaque panel on the back, helped to channel the seawater flow through the flume and aided in viewing of the CO₂ pool under the various stresses. Power and control of the benthic flume was achieved via the ROV by using an underwater mateable connection.

c. pH probes and calibration

SBE18 pH sensors (Seabird Electronics, Inc., Bellevue, WA 98005) were used. While these sensors have a nominal depth rating of 1200 m, we have found that when they are

Figure 2. The experimental flume being lowered into a test tank for velocity calibration of the thruster prior to the experiment. The thruster motor and impeller are at right. A honeycomb screen in front of the thruster helps provide a more laminar flow field. The velocimeter used for calibration is at the far left.

slowly deployed to depth, they can be used as deep as 4000 m. The pH electrodes were calibrated using seawater solutions where the pH had been previously adjusted using concentrated HCl or NaOH to ~ 6 and ~ 8 as measured by an IQ240 ISFET pH electrode (IQ Scientific Instruments, Inc., San Diego, CA 92127) that was calibrated using commercially available NBS pH standard solutions.

d. Seawater recirculation chamber

A small volume (~ 300 mL) chamber (Fig. 12) was equipped with both a pH sensor and a temperature sensor so that samples of CO_2 -enriched seawater could be collected and re-circulated. This allowed the *in situ* rate of the CO_2 hydration reaction to be studied. A Seabird submersible pump was used to fill, flush and re-circulate seawater in the chamber. Pumping rates on the order of 0.9–1.2 L/min were achieved at depth.

3. Experimental deployment and operation

The experiment carried out is simple in concept but difficult to execute. The work was carried out over a 3-day period from 25–27 October, 2003. Day 1 was devoted to deploying the sea floor flume and CTD-pH sensors, partially filling the flume with CO_2 , and testing the wave actuator and thruster. Day 2 was devoted to an extended series of wave generation

and water flow experiments. Day 3 was devoted to finalizing the fluid and plume tests, and safe recovery of the equipment.

a. Deployment

The complex set of equipment, including the flume, and recording CTD-pH frames, was deployed on a large “elevator” equipped with an acoustic beacon, and with floatation adjusted to sink at a speed of a few meters per minute. This was allowed to sink in free fall to the bottom at 3941 m depth. This was followed by an ROV dive, and acoustic location of the deployed material, which was found buoyed upright on a relatively flat sea floor. The equipment was removed from the elevator by a series of ROV manipulator operations and set up on the sea floor with the long axis of the flume in line with the observed local current, and the thruster motor upstream. The three recording CTD frames were placed in line downstream of the flume, slightly offset from each other in an effort to avoid shielding of the flow by the measurement structure. The frame placing was: Unit 1 = 0.5 m from the end of the CO₂ flume, Unit 2 = 2 m distant, and Unit 3 = 5 m distant. The local environmental conditions remained stable during the course of the experiment at $S_{\text{‰}} = 34.568$, and $T = 1.492^{\circ}\text{C}$.

b. Filling

The flume was partially filled with 40 L liquid CO₂ on day 1 of the experiment following procedures detailed in Peltzer *et al.* (2004) to ensure maximum delivered volume. The filling was completed with a second delivery on day 2, whereupon the CO₂ surface was approximately 5 cm below the lowest side of the flume.

c. Formation of a plume

The liquid CO₂ surface was investigated in three modes during the experiment.

- (1) Quiescent, with only local ocean water motions producing the plume. This replicates to some extent the results from the sea floor CO₂ experiments reported in Barry *et al.* (2004), and it is the condition recorded during the night hours when the vehicle was not present. The pH signal at a point records the plume only when the local current directs it by the sensor.
- (2) With gravity waves generated at the CO₂ surface by a flapper. This does not cause a directional plume, and these data are not the primary focus of this paper.
- (3) With seawater forced over the surface at varying speeds as controlled by the thruster motor. The thruster/flume system was calibrated in a test tank at one atmosphere and room temperature several days before deployment. The calibration data are shown in Figure 3.

Figure 3. Test tank calibration data for the thruster/flume system used for the experiments. The average velocities for several minute integrals were measured with a rapid response acoustic current meter for applied thruster speed (rpm).

4. Results

Although three experimental days were available, a technical error in setting the CTD-pH unit recording rates led to premature memory filling and only 2 days of plume sensing with the recording CTD systems were obtained, albeit at high temporal resolution.

a. Observing the liquid CO₂ surface processes

The boundary layer processes were observed in four ways: visually with the ROV camera, by careful placement of a pH electrode controlled by the vehicle robotic arm, by pH sensitive dye injection, and by water sampling.

- (i) The visual observation of the surface showed the pronounced effect of the wave motions created both by the flapper and thruster systems. The fluid dynamical analysis of the motions induced is discussed in a separate paper by Hove and Haugan (2005). We were careful not to exceed the critical velocity at which droplets of liquid were torn from the surface and advected past the downstream sensors. These can collect as a pool on the sea floor adjacent to the sensors.

We were routinely able to observe the formation of a hydrate skin on the liquid surface. Most often a thin skin of hydrate formed upon a globule of liquid CO₂, and the resulting increase in density was very small. Moreover full hydrate cage occupancy is difficult to achieve, and vacant cages produce a positive buoyancy

Figure 4A. Record of experimental probing of the static CO₂ boundary layer in the flume. The electrode is moved up and down in series of motions covering background seawater ~8 cm above the liquid surface (pH = 7.8) to actual probe contact (pH < 3.0). pH values of less than 3 are artifacts of contact with the nonaqueous surface and are not valid.

effect. We observed a raft of floating hydrate due to these effects forming at the downstream end of the flume in all our experiments. As the current velocity increased, the liquid surface showed no visual sign of hydrate presence, suggesting that the nucleation rate was slower than the rate at which fresh liquid CO₂ was supplied to the interface. As soon as the flow was turned off an opaque skin of hydrate propagated along the surface from the downstream end where the mass of hydrate had accumulated.

- (ii) The conventional tool for probing the plume is a glass pH electrode. Profiling with a pH electrode above the CO₂ pool was carried out by carefully positioning the sensor with the vehicle robotic arm. This was challenging for vehicle ergonomic reasons; it was not possible to have calibrated movement and positioning, and thus the distance between electrode tip and liquid CO₂ surface was obtained from post-cruise analysis of the video images. The record obtained from probing the boundary layer in the static condition after an overnight, unperturbed, period is shown in Figures 4A and B. Only background ocean values of pH (7.72) are observed until the electrode is within 1 cm of the CO₂ surface. On touching the liquid CO₂ surface (and presumably trapping a thin aqueous boundary layer at the electrode surface) pH values of 4 were recorded. By pressing the electrode into the pool, thus creating a depression in the surface filled with CO₂-enriched seawater, a

Figure 4B. Data selected from Figure 4A showing the accumulated record of pH versus distance to the liquid CO₂ surface. The low pH boundary layer, even under very low flow conditions is <1 cm thick; the sensor only responds to the change in hydrogen ion concentration, and does not detect the free CO₂ molecule.

pH as low as 3 was recorded. It is very likely that the influence of the nonaqueous liquid CO₂ surface was affecting the electrode readings, and that these cannot be regarded as true pH values. Rather they are indicators of strong gradients present in a very thin boundary layer.

- (iii) Injection of a phenol red indicator into the water flowing through the thruster allowed us both to visualize the flow rates and turbulence in the plume, and the pH changes occurring along the length of the flume surface (Fig. 5). It was not possible to recover from the color camera digital record quantitative estimates of the actual pH values. The qualitative signal showed a thin boundary layer over the CO₂ surface, with gradually changing color of the indicator as it flowed along the liquid CO₂ surface. As the dye stream reached the end of the flume and was mixed upwards into normal seawater on meeting the end wall a strong color change was observed (Fig. 5).
- (iv) Micro-sampling of the aqueous boundary layer was attempted. We built a unit of 3 evacuated stainless steel cylinders (50 ml volume) with a 5-port sampling valve. A hydraulically-driven cam controlled by the vehicle rotated the valve. The stainless steel capillary inlet tube, located near the tip of the pH probe (Fig. 6), was placed close to the CO₂ surface and the sampler was activated. Background ocean TCO₂

Figure 5. pH sensitive dye injection into the flume with water velocity $\cong 10$ cm/sec. The yellow dye indicating the low pH boundary layer is being mixed into normal seawater as it exits the end of the flume, and changing to red due to mixing with background ocean water. The dye changes color over the range 8.0 (red) to 6.6 (yellow).

values were obtained from 2 Niskin bottles attached to the vehicle; the average of the six samples obtained was $2342 \mu\text{mol/kg}$.

A total of nine boundary layer samples were obtained for shore-based analysis, with the highest value being only $2391 \mu\text{mol/kg}$. These small CO_2 enrichments observed are explained by extensive entrainment of surrounding water on opening the evacuated cylinders with a pressure differential of ~ 400 bars.

b. Observing the plume

The primary data set for observing the plume comes from the pH sensors placed ~ 50 cm beyond the downstream end of the flume. Those results are shown in Figure 7. The low electrical and thermal noise environment of the deep sea can yield extraordinarily stable *in situ* pH measurements (Brewer *et al.*, 2000). But the results downstream of a CO_2 source (Brewer *et al.*, 2004) and shown here in Figure 7, exhibit rapid changes far larger than can be attributed to turbulence alone. The relationship between applied thruster power and observed current speed (Fig. 3) is very well defined, but the series of velocity/pH tests

Figure 6. The evacuated stainless steel cylinder water sampling apparatus, held in the vehicle arm. The fluid intake tube is positioned at the tip of the pH electrode, close to the CO_2 surface.

embedded in Figure 7 show no simple correlation, and we seek answers for this complex behavior.

5. Discussion

The challenge of this experiment is to observe and understand the behavior of a plume of CO_2 rich seawater emanating from a lake of CO_2 placed upon the deep ocean floor. Of the several approaches tried here the only widely accepted one at this time is direct pH sensing, yet the observations shown in Figure 7 are unusual and indicate caution in interpretation.

The problem is that we do not yet have a sensor for the CO_2 molecule itself. We have visual observations of the liquid surface, but not of the dissolved CO_2 state. We have pH sensors for recording changes in hydrogen ion concentration, and we have conductivity sensors for recording changes in conductance. The relationship of each of these to the CO_2 system state is complex. Moreover, in Brewer *et al.* (2004) we drew attention to the problem that local disequilibrium in the near field CO_2 system might occur due to the well-known slow hydration kinetics (Johnson, 1982; Soli and Byrne, 2002). Here we investigate this problem further.

Figure 7. The complete pH record from Frame 1, placed within 50 cm of the end of the flume, with 3 electrodes (data offset for clarity) for the entire experimental period. The smaller perturbations in the center are from natural forcing of flow in the overnight period when the vehicle was not present. The largest signals result from forcing high velocities over the liquid CO₂ surface. The record at the far left is that during passive descent from the surface. The overshoot in pH is an artifact produced by the large and rapid changes in P and T during descent. The electrodes then stabilize at the sea floor conditions. The first series of pH spikes correspond to forced flows of 110 rpm, 1502 rpm, and 95 rpm producing a turbulent flow of low pH water as in Brewer *et al.* (2004).

a. Direct observations of CO₂ system disequilibrium

We have used the flow through pH cell (Fig. 12) to trap a volume of seawater in the flow loop to observe the stability of the plume signal. The cell intake tube was held in the vehicle arm and positioned in the flow field so as to draw in water at the desired location in the plume. The valves are operated hydraulically, the total system volume is about 460 ml, and the flow rate of the pump is about 2 L/min. In Figure 13 we show the results of two experiments with this system. In each case there is a rapid drop in pH from the oceanic background value of 7.88, and from the unstable plume signal of about 7.6, to a new stable reading of ~6.8. The drop in pH is extraordinarily rapid, and the new equilibrium value is reached in about 30 seconds.

Figure 8. The pH record from Cage 1 closest to the liquid CO₂ source during the unforced low flow (nighttime) period, data offset for clarity. Here there is modest evidence for greater density in the plume with the lowest placed sensor recording a bigger pH signal than the upper one. The middle sensor, placed at the height of the CO₂ surface, records the greatest signal.

b. Sensing of the plume-pH and conductivity

The above observation of significant disequilibrium in the plume CO₂ system is also apparent in the comparison of the pH and conductivity records obtained. The record of plume advection past the pH sensors deployed at the end of the flume is shown in Figures 7 and 8. The three pH sensors on each frame record hydrogen ion concentration, but the single conductivity sensor also records the events as perturbations to the local conductivity as water rich in a complex mixture of CO₂ system species flows by. In Figure 9 we show a fragment of the data (for clarity) in which the conductivity signal is also displayed. It is clear that although the electrode records a drop in pH, and therefore an increase in HCO₃⁻, the equivalent conductivity shows a decrease. The effect of added HCO₃⁻ is to increase conductivity (Brewer and Bradshaw, 1975); that effect is apparently being offset by a larger opposing signal of an undissociated (nonconducting) species.

However we also observe some large pH spikes with no equally large change in conductivity and the signals are therefore confusing. This is consistent with the flow cell experiments, and it must result from the passage of parcels of water with different time histories and thus different degrees of hydration as they flow by the sensors. What is most unusual is the rapidity of these changes.

Figure 9. A brief fragment of the pH and conductivity (expressed as salinity) record obtained from CTD 1 placed closest to the CO₂ source. In each case a low pH spike is accompanied by a decrease in conductivity. This indicates a mixture of CO₂(aq) and HCO₃⁻ species in the plume, with the CO₂(aq) being the dominant signal. This results from slow hydration kinetics of the CO₂ molecule in seawater.

c. Comparison of the pH and conductivity records

In contrast to the brief pH flow cell experiment, the signals recorded on the paired pH and conductivity sensors (Fig. 9) cover a large part of the observing period. In order to recover information from these complex signals of a rapidly fluctuating field we must make some approximations.

(i) The theoretical analysis of the conductivity changes in seawater from the CO₂ system was reported by Brewer and Bradshaw (1975). The basis for calculating the change in conductivity is to use the partial equivalent conductances (Λ_i) of the appropriate chemical species where

$$\Lambda_i = 1000\nu\delta K/\delta C_i + ViK \quad (1)$$

where ν is the specific volume of the solution reported, K is the electrical conductivity, and Vi and C_i are the partial equivalent volume and concentration of the added electrolyte i .

At equilibrium the primary effect of adding small quantities of CO₂ to normal seawater is to consume carbonate ion and produce bicarbonate as in:

A change in conductance of seawater by 2.5% corresponds to a 1‰ salinity change. For the addition of small quantities of CO_2 to seawater, with full conversion to bicarbonate ion, Brewer and Bradshaw (1975) give

$$\Delta\text{‰} = 0.030 \text{ per mmol CO}_2/\text{kg} \quad (3)$$

with the increase in bicarbonate ion producing an increase in conductivity.

But the increases in TCO_2 produced here are large, and the small quantities of $\text{CO}_3^{=}$ are soon overwhelmed (Fig. 9). The reaction is then simply

Substituting the value for $\Lambda_{\text{NaHCO}_3-}$ from Connors and Weyl (1968) we then find that

$$\Delta S\text{‰} = 0.060 \text{ per mmol CO}_2/\text{kg} \quad (4)$$

and we use this value as a useful approximation for our analysis of the data.

If equilibrium is not achieved, and the dominant species is undissociated CO_2 (aq) then the effect is to dilute the salts passing by the sensor; in normal deep seawater dissolved silicate and the atmospheric gases show this effect (Brewer and Bradshaw, 1975). It is not possible to distinguish between the undissociated species CO_2 (aq) and H_2CO_3 and these are commonly summed as the concentration of a hypothetical species, CO_2^* (Lueker *et al.*, 2000). The conductance effect is due to the volume fraction (ϕ) of the obstructing electrolyte, and the ratio Λ/Λ° lies between the limits $1 - \phi/2$ and $1 - 5\phi/2$, with the latter being the value for simultaneous validity of Stokes' Law and Einstein's equation for the viscosity (Stokes and Mills, 1965).

A numerical estimate of ϕ for CO_2^* in seawater is not available, nor is any information on the effect of pressure on this quantity. The effect on conductance of the normal atmospheric gases (N_2 , O_2) is $\sim 1.02 \times 10^{-5} \text{ ohm}^{-1} \text{ cm}^{-1}/\text{mmol/kg}$, or a change of $-0.02\text{‰}/\text{mmol/kg}$, and thus if we assume a similar relationship for the un-hydrated CO_2 molecule then a -1% change in conductivity indicates a change of ~ 50 millimolar CO_2^* passing by the sensor.

If the fluid passing by our sensor is close to equilibrium we will see a lowering of pH and an increase in conductivity. If the plume is far from equilibrium we will see a drop in pH from the fraction of CO_2 that has become ionized, but a decrease in conductivity from the dilution effect of the larger quantity of CO_2^* . The signals we observe fall between these extremes, depending upon the travel time to the sensors. We use these relationships here to examine the data obtained from the pH and conductivity record of the experiment. We cannot expect the sensors to have truly identical records of the plume; the single conductivity sensor is in an actively pumped flow, and the three pH electrodes are simply passively exposed. However the experimental arrangement was such that the tip of the middle electrode was placed very close to the intake tube of the CTD cell.

The change in total CO_2 content of the water flowing past the conductivity and pH sensors may then be approximated by combining the results as in:

$$\Delta\text{TCO}_2 = \Delta\text{HCO}_3^- + \Delta\text{CO}_2^*. \quad (5)$$

The term ΔHCO_3^- may be obtained conventionally from the alkalinity and observed pH data as in:

$$\Delta\text{HCO}_3^- = \frac{\Delta\text{pH}_{\text{measured}}}{\left(\frac{\delta\text{pH}}{\delta\text{HCO}_3^-}\right)_{\text{calculated}}} \quad (6)$$

and the conductivity data is a function of the two competing effects:

$$\Delta\text{Cond}_{\text{measured}} = \left(\frac{\delta\text{Cond}}{\delta\text{HCO}_3^-}\right) \times \Delta\text{HCO}_3^- + \left(\frac{\delta\text{Cond}}{\delta\text{CO}_2^*}\right) \times \Delta\text{CO}_2^*. \quad (7)$$

The quantities in the parentheses are known relationships from Eqs. 1–4 above, and $\Delta\text{pH}_{\text{measured}}$ and $\Delta\text{Cond}_{\text{measured}}$ are the data. The relationship $\delta\text{pH}/\delta\text{HCO}_3^-$ is known from the standard CO₂ system equations. There are three unknowns (ΔTCO_2 , ΔCO_2^* , and ΔHCO_3^-), so a solution is possible.

The strategy was to take the observed pH change, and calculate the change in HCO_3^- . We then use the relationship between conductivity and ΔHCO_3^- to estimate the increase in conductance caused by this species. We then take the observed change (decrease) in conductivity and compute the concentration of CO_2^* by summing the two contributions. We then estimated the total CO₂ increase in seawater flowing past the sensor by adding the ΔHCO_3^- and ΔCO_2^* contributions. The records of the individual ΔHCO_3^- and ΔCO_2^* contributions are shown in Figure 11.

d. The effects and implications of non-equilibrium conditions

The presence of strong local CO₂ disequilibrium effects was predicted and observed, by the contrasting pH and conductivity record. At 2°C and one atmosphere the e-folding time for CO₂ hydration predicted from the one atmosphere data is 303 seconds, and for dehydration it is 0.37 seconds, thus it is the hydration rate that provides the dominant effect. The result is that the observed boundary layer density is by no means as high as predicted from equilibrium models. Although the partial molal volume of CO₂ is reported as only 31 cm³ per mol, that value is only achieved after complete reaction with seawater and full hydration. The true partial molal volume of the unhydrated species is, as mentioned earlier, unknown, since observations of the CO₂ system at dis-equilibrium have not been made.

For advection of water across very large-scale lakes of CO₂ on the ocean floor the increased time scale would move the system closer to equilibrium as plume reactions occur, and the strong density increase predicted and modeled (Fer and Haugan, 2003) would likely be observed.

Our observations also suggest a previously unknown pressure effect on the CO₂ system rate constants in seawater, for although disequilibrium was observed the effects were less

Figure 10. Relationship between the change in pH and the change in TCO₂ for seawater at the temperature, pressure, and alkalinity of the experimental site. The change in slope near zero ΔpH is from consumption of the $\text{CO}_3^{=}$ ion; once that is removed the slope observed is simply due to HCO_3^- formation.

striking than estimated from the one atmosphere data. We will address this topic in a later study. Such a pressure dependence may be implied simply by the existence of the volume decrease on hydration of the CO_2 molecule, but possible energy barriers are unknown, and while the pressure dependence of the equilibrium state can be calculated from the partial molal volumes, the rate of change of a reaction can only be determined experimentally.

6. Summary and conclusions

We have carried out a novel experiment to investigate the formation of a plume of high CO_2 water emanating from a pool of liquid CO_2 on the ocean floor. The plume formation was induced by forcing water flow over the surface of the liquid with a controllable thruster. There have been many models and descriptions of this process in the context of deep ocean fossil fuel CO_2 disposal. Our initial findings substantially modify many of the concepts of such a system. Although the system is far inside the hydrate phase space we did

Figure 11. The record of ΔCO_2^* deduced from the conductivity record, and the change in HCO_3^- as recorded by the middle pH sensor. The ΔCO_2^* signal has been offset by 500 $\mu\text{mol/kg}$ for clarity. Both sensors are about 30 cm distant from the CO₂ source. The ΔCO_2^* signal clearly dominates, and the ratio will shift downstream as the hydration-ionization process occurs.

not observe large-scale hydrate formation, even under strong physical forcing which induced shearing of the liquid CO₂ interface. Although the density of the CO₂ hydrate is greater than that of the liquid, surface tension forces held what were essentially large globules of the liquid encased in a deformable hydrate skin floating on the liquid surface.

The plume was sensed by both pH electrodes, and by a conductivity sensor. The slow hydration rate of the CO₂ molecule resulted in very large amounts of CO₂ being undetected by the pH electrode, and the far larger component of the near field plume was detected by a drop in conductivity from dilution of sea salt by the unionized CO₂^{*} species.

While the slow hydration rate was clearly a major factor, the ΔpH observed was significant, and this hints at a pressure dependence of the hydration rate constants so that the rate is increased at high pressure. This may be expected from the large decrease in volume for the reaction, but it has not previously been observed.

The total quantity of CO₂ was estimated by converting the observed ΔpH into HCO_3^- , and calculating the increase in conductance contributed by this species. This was then

Figure 12. The looped flow cell used for observing disequilibrium in the CO_2 rich plume. The pH electrode is at left, with the sensor positioned within the flow cell. At center is the pump to provide flow, and two hydraulically controlled valves are at right. These are opened to draw in local seawater which passes by the electrode; closing the valves contains the sample in the flow loop, and allows observation of the time taken to reach equilibrium. The intake tube is stowed in a quiver seen at the far upper right. It is held in the vehicle arm and positioned at the desired location in the flow field.

combined with the decrease in conductance from the unionized molecule to yield a reasonable approximation for the plume signal.

The implications for monitoring a large-scale system are substantial. The use of pH sensors alone will not yield a complete signal, and is likely to underestimate the CO_2 signal in the near field. A sensor for the CO_2 molecule itself would be a great advantage, and newly developed *in situ* laser Raman spectrometers hold great promise for this (Brewer *et al.*, 2004; Pasteris *et al.*, 2004; White *et al.*, 2005).

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Figure 13. The record of pH from two looped flow experiments carried out on water samples from the CO₂ rich plume. At point A above the flow regime the normal quiescent ocean background signal of 7.88 is observed. The intake tube is then lowered into the flow regime, and large rapidly varying pH signals are observed at point B. Upon closure of the valves the pH signal quickly drops to a pH of 6.8 in region C, and very stable readings are recorded. The sequence is repeated by opening the flow loop, recording once again higher, and rapidly varying, pH signals (D). Upon valve closure the pH again drops (E), and upon raising the intake tube into background seawater and opening the valves normal and stable ocean values are recorded (F). The scale marks on the x-axis are 3 minutes, and the drop to an equilibrium value in the cell takes about 30 seconds.

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Seeing a Deep Ocean CO₂ Enrichment Experiment in a New Light: Laser Raman Detection of Dissolved CO₂ in Seawater

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We used a newly developed in situ laser Raman spectrometer (LRS) for detection of elevated levels of dissolved CO₂ in seawater. The experiment was carried out at 500 m depth, 6 °C, to examine new protocols for detection of CO₂-enriched seawater emanating from a liquid CO₂ source in the ocean, and to determine current detection limits under field conditions. A system of two interconnected 5 L chambers was built, with flow between them controlled by a valve and pump system, and this unit was mounted on an ROV. The first chamber was fitted with a pH electrode and the optical probe of the LRS. In the second chamber ~580 mL of liquid CO₂ was introduced. Dissolution of CO₂ across the CO₂–seawater interface then occurred, the valves were opened, and a fixed volume of low-pH/CO₂-enriched seawater was transferred to the first chamber for combined pH/Raman sensing, where we estimate a mean dissolution rate of ~0.5 (μmol/cm²)/s. This sequence was repeated, resulting in measurement of a progressively CO₂ enriched seawater sample. The rapid in-growth of CO₂ was readily detected as the Fermi dyad of the dissolved state with a detection limit of ~10 mM with spectral acquisition times of 150 s. The detection of background levels of CO₂ species in seawater (~2.2 mM, dominantly HCO₃⁻) will require an improvement in instrument sensitivity by a factor of 5–10, which could be obtained by the use of a liquid core waveguide.

Introduction

The rapid development of laser Raman spectrometers (LRSs) for deep-sea science (1, 2) provides new opportunities for advanced sensing of chemical processes in the ocean, with applications to methane hydrates, hydrothermal vent minerals and fluids, and gas fractionation studies, all now in progress.

Raman detection of the oceanic CO₂ system (TCO₂ = CO₂(aq) + H₂CO₃ + HCO₃⁻ + CO₃²⁻) provides a particularly attractive target, with the unique promise of separate detection of the CO₂ system species, since each has a characteristic spectroscopic signal (3, 4). In an early deployment of a deep-sea LRS system, Brewer et al. (1) successfully acquired a Raman spectrum from a pool of liquid CO₂ on the seafloor at 3600 m depth. However, the natural levels of CO₂ in the ocean are typically too low ([TCO₂] ≈ 2–2.5 mM) to

detect with current instrument sensitivity. Nevertheless, there are significant opportunities for signal enhancement (5–7), and there are also occasions where strongly elevated CO₂ levels can occur. These can be either man-made, as with the ocean sequestration of CO₂ (8–10), or natural deep-sea volcanic sources, including both the direct venting of liquid CO₂ from the seafloor (11, 12) and hydrothermal vent sites, where end-member fluids typically have a [TCO₂] of 10–20 mM, and can reach a highly enriched [TCO₂] of 60–300 mM in back-arc or hot-spot locations (13).

Under CO₂-enriched conditions, the lowered seawater pH perturbs the normal partitioning of the oceanic CO₂ system (with HCO₃⁻ as the predominant species), and dissolved CO₂ (CO₂* = CO₂(aq) + H₂CO₃) becomes dominant. The deep ocean is a cold, high-pressure environment, and at low temperatures the hydration rate of CO₂ in seawater is slow (14, 15). A pH electrode senses only hydrogen ions, and thus will not detect the dissolved molecular CO₂ signal until after the hydration step, and subsequent rapid deprotonation steps, is complete. This can result in underestimation of the true dissolved CO₂ burden, and such an instance has been reported (10) where, close to a liquid CO₂ source at 3960 m depth, pH measurements greatly underestimated the near-field dissolved CO₂ signal, and corrections were made by observing the reduction in conductivity caused by the large quantity of nonionic species flowing by the sensor.

The ability to acquire in situ data allowing a direct quantitative assessment of carbonate speciation would present a powerful new tool to the oceanographic community, and this has attracted the attention of many researchers, with numerous studies on aqueous CO₂ and simple alkali-metal bicarbonate and carbonate solutions (4, 5, 16–18). Davis and Oliver (4) determined the molecular symmetry of aqueous CO₂, bicarbonate ion, and carbonate ion in relatively concentrated aqueous media (CO₂(g) at 5 atm in equilibrium with H₂O, and HCO₃⁻ and CO₃²⁻ at 0.2–8 M). The authors noted the appearance of a carbonate band in a KHCO₃ solution, and conducted a simple titration experiment that clearly demonstrated Raman detection of the shift in equilibrium position from the bicarbonate to carbonate ion as the pH increased. This study was followed by the first steps toward examination of the CO₂ system in natural waters, with analysis of more dilute solutions to a lower limit of 100 mM (16). More recently, Raman studies of the CO₂ system speciation in synthetic hydrothermal solutions (1 M HCO₃⁻ and CO₃²⁻, 22–550 °C, 100–200 dbar) have been used to investigate the accuracy of, and provide essential experimental data for, theoretical thermodynamic models of this complicated system (18). Although these studies have provided valuable fundamental information on the aqueous CO₂ system, no field applications have yet been carried out.

Information on the dissolution rate of liquid CO₂ in seawater at depth is also needed as input for the design of free ocean CO₂-enrichment (FOCE) experiments, in which it is envisioned that CO₂ is added to seawater in a controlled fashion to create a local environment that simulates the anticipated high-[CO₂]-low-pH characteristics of the ocean during the latter part of the 21st century (19, 20). Such a procedure is technically challenging, and will most likely require formation of a precursor CO₂-enriched fluid (of known concentration) within a reaction vessel under strictly controlled conditions, as opposed to simple injection of CO₂ into the FOCE control zone.

Here we present results of Raman detection of CO₂ dissolving into seawater at 500 m depth and 6 °C, and a determination of the current in situ detection limits. These

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may differ from laboratory detection limits due to the combined effects of pressure and temperature on the fully assembled sea-going spectrometer system. We also use pH measurements to estimate the dissolution rate of CO₂ into seawater within a dual-chamber reaction vessel designed to minimize hydrate formation during the production of CO₂-enriched seawater.

Experimental Section

Laser Raman System. We used the deep-ocean Raman in situ spectrometer (DORISS) (1, 2), with modifications as described by White et al. (21). DORISS is a laboratory model laser Raman spectrometer (LRS) from Kaiser Optical Systems, Inc. (KOSI), adapted for use in the deep sea to depths as great as 4000 m. The instrument consists of a 532 nm Nd:YAG laser, a holographically filtered probe head with interchangeable optics, a holographic duplex grating, and a 512 × 2048 front-illuminated CCD camera from Andor Technology. The duplex grating splits the spectrum into two stripes on the face of the CCD chip, providing a spectral range of 100–4400 Δcm^{-1} with a digital resolution of $\sim 1 \Delta\text{cm}^{-1}$ per pixel. An immersion optic with an $f/2$ lens at the end of a 25 cm metal tube sealed with a sapphire pressure window (rated to 3000 psi) was used for this experiment. The working distance (from sapphire window to focal point) of this optic is 4 mm in seawater.

The spectrometer was calibrated on deck immediately prior to deployment, using a neon lamp for wavelength calibration, and a calibrated tungsten lamp for intensity. The laser wavelength was calibrated against the 801 Δcm^{-1} Raman line of cyclohexane (22). A small diamond plate was placed inside the probe head in the laser beam path, so that the 1332 Δcm^{-1} diamond Raman line is superimposed on all acquired spectra. This also provides a wavelength reference standard (1, 23). The full width at half-maximum (fwhm) height of the sharpest lines in the neon spectrum was $\sim 3.7 \Delta\text{cm}^{-1}$, giving a spectral resolution of $\sim 4.6 \text{ cm}^{-1}$ (according to the Rayleigh criterion) for this deployment. The laser power output, measured at the focal point of the immersion optic prior to deployment, was ~ 28 mW. Spectra were acquired using KOSI's HoloGRAMS software, where dark spectrum subtraction and wavelength and intensity correction were performed by HoloGRAMS during acquisition and the processed spectra were saved in generic spectrum (.spc) format.

Apparatus. A system of two interconnected 4.95 L cylindrical acrylic chambers was built, with flow between them controlled by a valve and pump system (Figure 1). The internal volume of the associated valves and tubing was approximately 100 mL, giving a total system volume of ~ 10 L.

The first, or measurement, chamber was equipped with a thermistor for logging temperature and a pressure-balanced glass combination pH electrode (Ag/AgCl reference probe, Seabird Electronics, Inc., SBE-18), modified by the manufacturer to be deployed at depth. The output from the pH electrode is internally amplified and offset to yield an analogue output signal voltage between 0 and 5 V. The pH probes were calibrated using seawater solutions where the pH had been previously adjusted using concentrated HCl or NaOH to ~ 6 and ~ 8 as measured by an IQ240 ISFET pH electrode (IQ Scientific Instruments) that was calibrated using commercially available NBS pH standard solutions. The Raman immersion optic was inserted horizontally into this chamber, such that the focal point of the optic was positioned at the same height as the pH electrode tip and approximately in the center of the chamber volume.

The second, or dissolution, chamber was equipped with a thermistor at the base and the CO₂ inlet at the top. This chamber was also fitted with hydraulically controlled ports

FIGURE 1. Schematic showing the experimental apparatus used for combined Raman and pH sensing of CO₂-enriched seawater at 500 m depth on the ROV *Ventana*. Squares represent hydraulically controlled valves (a square with “X” means the valve is closed). The flush and isolate valves each consist of three individual valves operated on the same hydraulic function. Valve positions are shown for deployment to allow flooding of the chambers with seawater during the ROV descent to 500 m.

for venting seawater (or CO₂) at both the top and bottom (“vent” valves). The liquid CO₂ was delivered from a 9 L accumulator mounted on the rear of *Ventana* following techniques described previously (9).

Ports entering and exiting from the sides of the acrylic chambers allowed circulation of seawater between the two chambers via nylon tubing (12.7 mm i.d.). A flow meter and Seabird 5T pump were positioned on the lower tubing path, such that the direction of pumped flow was from the lower port of the dissolution chamber to the lower port of the measurement chamber, with return flow above. The upper tubing path included a hydraulically controlled valve array (“flush” in Figure 1) to allow flushing of the system with ambient seawater. Another hydraulic valve array (“isolate” in Figure 1) between the upper and lower tubing paths allowed isolation of the dissolution chamber with continued circulation of fluid only through the measurement chamber. Both chambers were equipped with a capillary tube (0.5 mm i.d.), open to the ocean, to accommodate the volume changes.

The pH, thermistor, and flow sensor data were digitized and transmitted in real time via the ROV tether to the control room aboard the R/V Point Lobos and recorded.

Field Experiment. The experiment took place on May 9, 2005, at 500 m depth in Monterey Bay, CA, where the P – T environment ensured the liquid phase of CO₂ was within the CO₂ hydrate stability zone (8, 9). We used the ROV *Ventana* deployed by the RV *Point Lobos* as experimental platforms for equipment deployment and control. The DORISS probe-head pressure housing and the experimental apparatus were mounted on a rigid square bar across the front of the ROV, such that the apparatus was within the field of view of the main science camera on the ROV (Figure 2). Hydraulic actuation opened and closed the flush and isolate valve assemblies; both are shown in the open position in Figure 1. The viewing system on *Ventana* allowed for real-time observation of the experiment, providing visual confirmation of the CO₂ injection and hydraulic valve switching. All lights on the ROV were turned off while Raman spectra were collected; the light provided by the laser was sufficient to allow continued viewing of the experiment.

In our experience, the DORISS system shows some decrease in sensitivity in field deployments when compared to laboratory experiments, most easily recognized by a reduction in the total intensity (Raman peak area) of the water stretching band. This decrease in sensitivity is most likely due to the effect of pressure on the external fiber optic cables and to small changes in the optical path of the

FIGURE 2. Experimental apparatus mounted on the front of the ROV *Ventana*. The Measurement chamber is to the left, with the Raman probe head supported by the two black rings. The valve assembly is at the center, with the pump and flow meter extending down from the lower loop. The dissolution chamber is at the right, with the CO₂ introduction valve mounted on top of the chamber.

spectrometer from both pressure- and temperature-induced stresses. In the experiment reported here, seawater spectra acquired during the ROV descent indicate no signal loss between 100 and 300 m, and a loss of ~20% at 500 m depth.

Procedure. The procedure was to dive the vehicle to 500 m water depth, with the pump on and the flush, isolate, and vent valves open to allow flooding of the apparatus. At 500 m the two vent valves were closed, and the apparatus was flushed with ambient seawater until the temperature measured in both chambers was equal to the external ocean value. The flush and isolate valves were then closed, the pump was turned off, and a spectrum of the ambient seawater contained inside the measurement chamber was collected. The bottom vent valve on the dissolution chamber was then opened to allow displacement of seawater, and 580 mL (4.5 strokes of a 128 mL piston) of liquid CO₂ was injected into the dissolution chamber. Immediately following injection, the bottom vent valve was closed. At 500 m, liquid CO₂ is buoyant with respect to seawater, and thus formed a layer at the top of the chamber. Dissolution of CO₂ across this interface creates seawater strongly enriched in dissolved inorganic carbon (DIC) within the dissolution chamber. The CO₂ was allowed to dissolve for ~10 min. The pump was then turned on, and the following series of steps were repeated 15 times: (a) the isolate valve assembly was opened, allowing CO₂-enriched seawater to circulate between the dissolution chamber and the measurement chamber; (b) the isolate valve assembly was closed, and the CO₂-enriched fluid was recirculated through the measurement chamber to ensure good mixing; (c) the pH in the measurement chamber was used to monitor mixing, where the pH decreases as the added CO₂-enriched water becomes well mixed and equilibrates with the water initially held in the measurement chamber; (d) once the pH approached a constant value, a Raman spectrum of the CO₂-enriched fluid was obtained. Throughout these steps, CO₂ is continuously dissolving across the CO₂-seawater interface within the dissolution chamber. During step a, this occurs under vigorous flow conditions, which disturbed the CO₂-seawater interface. For steps b–d, dissolution occurs under static no-flow conditions. The flow rate was logged continuously, and the time of all valve switching was recorded accurately; thus, the volume of water pumped between the chambers, and the timing of each step, is well-known. For samples 1–11, the isolate valve was held open for ~1 min, exchanging ~1350 mL of water between the chambers. For samples 12–15, this was increased to ~2 min, exchanging ~2700 mL of water. A Raman spectrum of each sample was obtained with a total acquisition time of

TABLE 1. Summary of the Valve Status during the Experiment Procedures

procedure	flush	isolate	vent top	vent bottom	CO ₂ inlet
flooded apparatus during descent	open	open	open	open	closed
flushing with ambient seawater	open	open	closed	closed	closed
injection of liquid CO ₂	closed	closed	closed	open	open
pumping between chambers	closed	open	closed	closed	closed
recirculating in measurement chamber	closed	closed	closed	closed	closed

FIGURE 3. Flow meter and pH data over the course of the experiment. The vertical gray bars indicate the time of spectral acquisition. When the isolate valve is closed, a high flow rate of ~1.55 L/min is observed. When the isolate valve is open, a lower flow rate of ~1.35 L/min is observed.

150 s. The short time step between each sample point (chosen to allow clear observation of the in-growth of the CO₂ signal) did not permit replicate measurements to be made. However, at the end of the experiment triplicate measurements were made of the final sample S15, enabling an estimate of the instrument precision to be made.

The valve positions for all experimental procedures are summarized in Table 1. The logged flow meter and pH data, and the time of spectral acquisitions, are shown in Figure 3.

Results and Discussion

pH Signal. The raw sensor (electrode + preamplifier) output voltage obtained was converted to pH using the equation

$$\text{pH} = 7 + (V_{\text{out}} - \text{offset}) / (KT(\text{slope})) \quad (1)$$

where V_{out} is the pH electrode output voltage, $K = (R/F) \ln 10$, R is the gas constant ($8.3144 \text{ K}^{-1} \text{ mol}^{-1}$), F is the Faraday constant ($9.6485 \times 10^4 \text{ C mol}^{-1}$), and T is temperature in degrees kelvin.

The evolution of pH in the Raman chamber over the duration of the experiment is shown in Figure 3, and the average pH measured across each spectral acquisition is given in Table 2. The [TCO₂] and CO₂ system speciation at each spectral sampling point were calculated from the pH data, using version 1.05 of the CO2SYS software (24), using the carbonate equilibrium constants calculated by Dickson and Millero (25) on the basis of a refit of Mehrbach's data. Of the CO2SYS inputs, salinity (34.35), temperature (6 °C), and pressure (504.5 dbar) were measured in situ. The total alkalinity (TA; $2334 \mu\text{mol/kg}$), initial [TCO₂] ($2314 \mu\text{mol/kg}$), silicate concentration ($90.1 \mu\text{mol/kg}$), and phosphate concentration ($3.08 \mu\text{mol/kg}$) were interpolated as a function

TABLE 2. Measured pH and Calculated CO₂ System Concentrations in the Raman Chamber at Each Spectral Acquisition

sample	T (°C)	pH (NBS)	[TCO ₂] (±std dev) (μmol/kg)	[CO ₂ *] (μmol/ kg)	[HCO ₃ ⁻] (μmol/ kg)	[CO ₃ ²⁻] (μmol/ kg)
S0 (seawater)	5.97	7.708	2314 (2)	56	2210	48.0
S1	6.13	5.542	11050 (220)	8713	2336	0.3
S2	6.01	5.229	20330 (450)	17990	2340	0.2
S3	6.04	5.054	29320 (670)	26970	2343	0.1
S4	6.11	4.932	38090 (890)	35740	2346	0.1
S5	6.06	4.849	45640 (1070)	43290	2349	0.1
S6	6.02	4.766	54750 (1300)	52390	2352	0.1
S7	6.03	4.701	63350 (1510)	60990	2354	0.1
S8	6.10	4.646	71730 (1720)	69370	2357	0.0
S9	6.16	4.596	80270 (1930)	77910	2360	0.0
S10	6.18	4.550	88950 (2140)	86590	2363	0.0
S11	6.04	4.513	96630 (2330)	94270	2366	0.0
S12	5.98	4.459	109300 (2600)	106900	2370	0.0
S13	5.98	4.422	119300 (2900)	116900	2373	0.0
S14	5.98	4.391	128300 (3100)	125900	2376	0.0
S15	5.98	4.359	137900 (3400)	135500	2379	0.0

of σ_θ (27.06) from the WOCE P17N Station 10, 1993 data. The initial seawater pH (7.708) was calculated on the basis of these values. We estimate an uncertainty in the interpolated TA and initial [TCO₂] of ± 1 μmol/kg, giving an estimated uncertainty in the initial pH of ± 0.006 . This uncertainty is propagated through as an estimated uncertainty in [TCO₂] at each sample point, and is greater than the uncertainty due to a 1% error in the carbonate equilibrium constants K_1 and K_2 . The results of these calculations are given in Table 2.

Raman Signal: Spectral Processing. Spectral analysis was performed using GRAMS/AI data processing software (Thermo Electron Corp.). All spectra were smoothed using a single pass of the third-order Savitsky–Golay smoothing function, where the smoothing width was determined from the full width at half-maximum (fwhm_{min}) height of the narrowest peak requiring resolution (26):

$$\text{smoothing width} = 0.7(\text{fwhm}_{\min})/Y \quad (2)$$

where Y is the data resolution of the spectrum ($\Delta\text{cm}^{-1}/\text{data point} = 0.3$).

A conservative fwhm_{min} of ~ 7 Δcm^{-1} was used for the low-wavenumber region (0–2140 Δcm^{-1}). In the high-wavenumber region (2140–4400 Δcm^{-1}), an fwhm_{min} of 70 Δcm^{-1} was used, equal to the width of the narrowest peak in the water stretching band when deconvolved to five overlapping Gaussian peaks. Both the low- and high-wavenumber regions were baseline corrected using a two-point linear fit to the data.

The peak position (i.e., Raman shift), height, fwhm, and area were determined using the GRAMS/AI peak-fitting routine with a Gaussian peak shape. The spectra were integrated from 920 to 1040 Δcm^{-1} (sulfate), from 1200 to 1475 Δcm^{-1} (CO₂ peaks and reference diamond), and from 2700 to 3900 Δcm^{-1} (water stretching band).

The intensity of Raman scattering can be written in simple form as

$$R = IKP\sigma C \quad (3)$$

where R is the Raman peak area, I is the laser intensity, K includes instrument parameters such as optical transmission and collection efficiency, P is the sample path length, σ is the Raman cross-section or scattering efficiency of the species under investigation, and C is the concentration per unit volume (27). As parameters such as K and P may differ in the

FIGURE 4. Raman spectra of seawater (black) and CO₂-enriched seawater (dark gray). The high-wavenumber region contains the high-intensity water stretching band (3000–3600 Δcm^{-1}). The inset shows the expanded low-wavenumber region containing the SO₄²⁻ ν_1 peak (981 Δcm^{-1}), the CO₂ Fermi dyad (1274 and 1382 Δcm^{-1}), the reference diamond peak (1332 Δcm^{-1}), and the water ν_2 peak (1640 Δcm^{-1}). The difference spectrum (light gray, S15 – S0) shows only the CO₂ Fermi dyad.

collection of separate spectra, an internal reference standard is required. For this experiment, all spectra were normalized to a constant area under the water stretching band. The entire spectrum was multiplied by the normalization factor N :

$$N = X/R_{\text{H}_2\text{O}} \quad (4)$$

where X is an arbitrary constant and $R_{\text{H}_2\text{O}}$ is the Raman peak area of the water stretching band for that spectrum. If we then consider eq 1 for both an unknown sample peak and the water stretching band, we obtain the following equations:

$$R_{\text{unknown}}^* = NIKP\sigma_{\text{unknown}}C_{\text{unknown}} \quad (5)$$

$$R_{\text{H}_2\text{O}}^* = X = NIKP\sigma_{\text{H}_2\text{O}}C_{\text{H}_2\text{O}} \quad (6)$$

where R^* indicates the normalized peak area. As R_{unknown} and $R_{\text{H}_2\text{O}}$ are collected simultaneously, the term $NIKP$ is equal in eqs 3 and 4, and the following relationship can be obtained:

$$R_{\text{unknown}}^* = A(C_{\text{unknown}}/C_{\text{H}_2\text{O}}) \quad (7)$$

where A is constant across all spectra and equal to

$$A = R_{\text{H}_2\text{O}}^*(\sigma_{\text{unknown}}/\sigma_{\text{H}_2\text{O}}) \quad (8)$$

Thus, the normalized area of any unknown Raman peak is directly proportional to the ratio of the concentration of the unknown species to the concentration of water.

Raman Spectra of Seawater and CO₂(aq). The Raman spectra of ambient seawater (S0) and CO₂-enriched seawater (S15) are shown in Figure 4. The characteristic seawater peaks are due to the symmetric stretch of the sulfate ion (SO₄²⁻; $\nu_1 \approx 981$ Δcm^{-1}), and the water bending ($\nu_2 \approx 1640$ Δcm^{-1}) and stretching (3000–3800 Δcm^{-1}) modes. The water stretching band consists of a complex profile of several broad and overlapping peaks, where the relative intensity of these peaks is strongly dependent on the temperature and ions in solution (28, 29). No apparent difference in the shape of this band was seen between the spectra, consistent with the constant temperature of the experiment, and the small change in salinity (~ 1 unit overall; 10) due to dilution of seawater by the addition of a molecular species (TCO₂ is dominantly added as CO₂*; see Table 2), where the water:ion ratio remains unchanged. In the CO₂-enriched spectrum, the two additional

FIGURE 5. Raman spectra of the CO₂ Fermi dyad region for all samples (S0–S15). The diamond peak has been removed for clarity by setting the region from 1315 to 1350 Δcm⁻¹ to 0 (baseline). The CO₂ peaks are first observed in S2, where the increase in peak intensity from S2 to S15 as the seawater becomes progressively enriched in CO₂ can be clearly seen.

peaks of the CO₂ Fermi dyad (~1274 and ~1382 Δcm⁻¹), which result from a Fermi resonance between the 2 ν₂ and ν₁ peaks of the CO₂ molecule (3), are observed to either side of the reference diamond peak (~1332 Δcm⁻¹). Close examination of the low-wavenumber region reveals that no additional peaks are observed in any spectrum, and this was confirmed by obtaining difference spectra (S_{X,diff} = S_X – S₀). The difference spectrum for S15 is shown in the inset of Figure 4.

The low-wavenumber spectral region containing the CO₂ Fermi dyad for samples S0–S15 are displayed in stacked mode in Figure 5. The in-growth of CO₂ as dissolution progresses from ambient seawater (S0) to the most TCO₂ enriched sample (S15) can be clearly seen. The Raman peak position, height, and normalized area for the CO₂ peaks are presented in Table 3. The position of these peaks is relatively constant, with the smaller, low-wavenumber peak occurring at 1274.2 ± 0.9 Δcm⁻¹ (peak 1) and the larger, high-wavenumber peak at 1381.6 ± 0.3 Δcm⁻¹ (peak 2). Replicate measurements of S15 give an estimated precision in the normalized peak area of ±9% for peak 1 and ±2% for peak 2. The higher variation observed in both the position and normalized area of the first peak is attributed to an increased uncertainty due to the comparatively low peak intensity. The peak positions measured here agree well with previously published values for solution-phase CO₂ (1276 and 1384 Δcm⁻¹; 12), although there would appear to be a small decrease in peak frequency (~2 Δcm⁻¹) from the solution phase at 5 atm to the solution phase at 50 atm.

Combined pH and Raman Results and Raman Detection Limits. The integrated Raman peak areas for the CO₂ Fermi dyad (R_{p1}^* and R_{p2}^*) are plotted against the [CO₂*] determined from pH measurements in Figure 6. The area under the CO₂ peaks should be linearly related to the concentration ratio of aqueous CO₂ to H₂O (eq 7). However, the decrease in water concentration (due to dilution by CO₂*) is small, and may be considered negligible when compared to the large increase in [CO₂*] (Δ[H₂O] << Δ[CO₂*]). We therefore assume R_{p1}^* and R_{p2}^* are directly proportional to [CO₂*]. An excellent linear

TABLE 3. Measured Raman Peak Characteristics for the CO₂ Fermi Dyad

spectral sample	[CO ₂ *] (μmol/kg)	peak 1		peak 2	
		center X (Δcm ⁻¹)	area R_{p1}^*	center X (Δcm ⁻¹)	area R_{p2}^*
S0 (seawater)	56	nd	nd	nd	nd
S1	8710	nd	nd	nd	nd
S2	17990	1273.6	300	1381.3	1096
S3	26970	1274.2	442	1382.4	1683
S4	35740	1275.3	779	1381.1	2359
S5	43290	1276.1	807	1381.6	2827
S6	52390	1273.4	1172	1381.8	3680
S7	60990	1274.0	1516	1381.8	5226
S8	69370	1274.8	1647	1381.7	5463
S9	77910	1273.2	2234	1381.6	6189
S10	86590	1273.5	2085	1381.8	7342
S11	94270	1272.8	2636	1381.6	7790
S12	106900	1274.0	3042	1381.6	9026
S13	116900	1274.6	2978	1381.5	10385
S14	125900	1273.6	3690	1381.8	11363
S15a	135500	1274.5	3679	1381.5	12025
S15b	135500	1274.4	4102	1381.6	11608
S15c	135500	1274.7	3403	1381.5	11687

FIGURE 6. Normalized Raman peak areas for the CO₂ Fermi dyad plotted against calculated [CO₂*]. The model 2 linear fits (geometric mean regression) to the data are also shown.

relationship is observed between both R_{p1}^* and R_{p2}^* and [CO₂*], where model 2 linear regressions (geometric mean) yield the following relationships:

$$R_{p1}^* = 30.8C_{CO_2^*} - 384.2 \quad (9)$$

$$(r = 0.9887, \sigma_m = 1.23, \sigma_b = 113.0)$$

$$R_{p2}^* = 94.8C_{CO_2^*} - 972.5 \quad (10)$$

$$(r = 0.9977, \sigma_m = 1.70, \sigma_b = 155.8)$$

where $C_{CO_2^*}$ is in millimoles per kilogram. The excellent correlations observed clearly demonstrate that the novel application of in situ Raman spectroscopy provides quantitative data that compare very well with those of conventional pH sensing at equilibrium. These relationships indicate a detection limit, for this particular configuration and acquisition time, on the order of ~12.5 mmol/kg for peak 1 and ~10.3 mmol/kg for peak 2. This is consistent with the absence of CO₂ peaks in sample S1, where the CO₂* concentration was ~8.7 mmol/kg. The large negative y intercepts obtained in both regressions are most likely due to the peak-fitting

routine. In general, Raman peaks are best fit to a Lorentzian–Gaussian peak shape, where a high proportion of peak area is within the tails of the peak. However, for reasons of reproducibility, we chose to fit Gaussian peaks to the spectra, although this may result in a small underestimation of the total peak area.

We note that direct comparisons between detection of CO_2^* , HCO_3^- , and CO_3^{2-} should not be made due to different Raman scattering efficiencies of these species. Nevertheless, the detection limit determined here (~ 10 mM) significantly improves on previously reported Raman signal detection for the aqueous CO_2 system, and laboratory analysis has demonstrated that the current DORISS system allows direct detection (no advanced spectral processing) of 15 mM HCO_3^- , whereas the use of a new generation of advanced high-volume collection optics enables direct detection of 7 mM HCO_3^- (30). The present sensitivity of the DORISS instrument, although still too low for detection of oceanic background values, indicates that the application of the Raman technique appears very suitable for examination of natural deep-ocean volcanic CO_2 sources, where the CO_2 fluid signal is usually combined with elevated levels of other Raman-active species such as H_2S and CH_4 (11, 12).

Future Improvements. Our ultimate goal is to develop the use of in situ Raman spectroscopy to enable direct detection of ambient seawater CO_2 system speciation. To achieve this would require an improvement on current instrument sensitivity by a factor of 5–10, which should be readily attainable using well-known signal enhancement techniques such as the application of liquid core waveguides (LCWs).

Total reflection of light within an LCW increases the optical path length (i.e., the number of scattering centers sampled), and the application of LCWs has been widely demonstrated to greatly increase spectroscopic sensitivity by factors of 10–1000 (5–7). Song et al. (5) report a signal enhancement by a factor of ~ 20 for aqueous Na_2CO_3 using a 1 m Teflon-AF LCW and laser wavelength of 785 nm. Excitation at shorter wavelengths (e.g., DORISS laser wavelength of 532 nm) is expected to give significantly higher transmission efficiency in aqueous solution, leading to an effective higher enhancement of the Raman signal (5). Thus, it would appear that a 20-fold, or greater, improvement on current in situ Raman detection limits within the near future is realistic. If this is achieved, the Raman technique would allow direct detection of the individual components of the aqueous CO_2 system at natural background levels, in addition to observation of the extent of disequilibrium in CO_2 -enriched plumes emanating from either a sequestration experiment “disposal” site (10) or a natural seafloor vent site.

Dissolution Rate of Liquid CO_2 . The dissolution rate of liquid CO_2 can vary greatly with the vigor of mixing, which changes both the surface area exposed and the thickness of the diffusive boundary layer. In this experiment only slow mixing rates were intermittently applied, so any estimate will represent a low end member for the rate. We have made such a calculation as follows.

The $[\text{TCO}_2]$ (determined from pH measurements) in the measurement chamber at each sampling point, TM_S , is dependent on the $[\text{TCO}_2]$ for the previous sample point, TM_{S-1} , and the additional volume of CO_2 -enriched seawater transferred from the dissolution chamber. The $[\text{TCO}_2]$ of the seawater transferred from the dissolution chamber is considered to be the final concentration reached at the end of the previous dissolution step ($S-1 \rightarrow S$), TD_{S-1}^f . Fluid in the dissolution chamber is also replaced by less enriched fluid from the measurement chamber, such that the $[\text{TCO}_2]$ at the

start of the subsequent dissolution step ($S \rightarrow S+1$), TD_S^i , is reduced. These relationships are expressed in eqs 11 and 12,

$$\text{TD}_{S-1}^f = \frac{V_M \text{TM}_S - (V_M - E_S) \text{TM}_{S-1}}{E_S} \quad (11)$$

$$\text{TD}_{S-1}^i = \frac{(V_D - E_S)(V_M - E_S) \text{TD}_{S-1}^f + \text{TM}_{S-1}}{V_D} \quad (12)$$

where V_M is the volume of the measurement chamber (~ 5000 mL) and V_D is the volume of seawater in the dissolution chamber, assumed to be equal to the total volume minus the volume of liquid CO_2 (~ 4420 mL). E_S is the volume of fluid exchanged between the measurement and dissolution chambers prior to each sampling point, S , and can be accurately determined from the flow rate multiplied by the length of the exchange step. As a first approximation, we treat this transfer as occurring instantaneously at the midpoint of the exchange (t_S), where the length of the dissolution step, Δt_S , is then $t_S - t_{S-1}$.

These data give a mean dissolution rate of 12.5 ± 2.1 mmol/min (1σ), where the uncertainty primarily reflects the assumption of instantaneous transfer (with zero re-entrainment of water into the return flow back to the Raman chamber, and no account for changes in the dissolution regime under dynamic and static conditions). Consequently, this result represents an approximation, where the true dissolution rate under conditions of steady flow is likely to be moderately faster. The internal diameter of the CO_2 chamber is 22.9 cm. Assuming a planar circular interface (area ~ 410 cm²), this corresponds to a dissolution rate of ~ 0.50 ($\mu\text{mol}/\text{cm}^2/\text{s}$). This estimate is of the same order of magnitude as our previous determinations of the dissolution rate of CO_2 into seawater, both under static conditions at 3600 m water depth (1.7 ($\mu\text{mol}/\text{cm}^2/\text{s}$); 31) and under dynamic conditions as a plume of liquid CO_2 droplets rise through the water column from 800 m depth (3.0 ($\mu\text{mol}/\text{cm}^2/\text{s}$); 32).

The successful formation of highly CO_2 enriched seawater under controlled conditions at depth suggests that this fluid could be readily created in large quantity for oceanic perturbation experiments. The experiment we carried out took place well within the P – T conditions of CO_2 hydrate formation (8, 9), yet our design enabled us to carry out the work over several hours without interference from hydrate plugging of the system, or hydrate formation at the CO_2 –seawater interface, causing a sufficiently large barrier to the dissolution rate (33) that formation of a large volume of low-pH–high- $[\text{CO}_2]$ water was inhibited. This shows the importance of the injection technique in carrying out this class of work. If a high-velocity jet reactor is used (34) to force contact between droplets of CO_2 and water in the required 1:6 ratio, then a pastelike composite of CO_2 hydrate can be readily formed. In this case we placed the CO_2 injection point so that the inlet was kept immersed within the liquid CO_2 phase, where the very low solubility of water in CO_2 ensures that hydrate formation at the injection point did not occur.

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Free Ocean CO₂ Enrichment (FOCE) System: Technology for Chemical and Biological Studies of a High CO₂ Ocean

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Abstract – The burning of fossil fuels for energy production has produced cumulative emissions on the order of 1 trillion tons since the beginning of the industrial revolution. While approximately half of the CO₂ has remained in the atmosphere, most of the rest has been absorbed by the surface ocean. This has resulted in a lowering of the surface ocean pH by about 0.1 units and, if society is able to stabilize atmospheric CO₂ levels at twice the pre-industrial concentration, will result in a lowering of surface ocean pH by 0.25 units. While some researchers are asking the question of whether we should pursue direct ocean CO₂ sequestration, the FOCE experiment asks what the impact of this pH change will be on ocean biogeochemistry and ecology. In order to address this question, MBARI scientists and engineers have designed apparatus to enable small-scale in situ CO₂ enrichment experiments to be carried out, in a manner analogous to the land-based Free Air CO₂ Enrichment (FACE) experiments. The FOCE prototype was designed to test the ability to control pH within a fixed but freely exchanging volume of sea water. The technology concept for the experiment is based on a small ring structure using a central valve to direct the flow of pH altering fluid. The initial phase of the project uses concentrated HCl mixed with sea water and includes directional and volume control to achieve a desired pH offset. Control feedback is obtained by using pH sensors in the center of the control volume. Other aspects of the design that address the inherent time delays and noise of the associated pH signal are also discussed. Test results show the capability of the system to maintain closed loop control of pH in a given volume. Sea trials, at a selected site, then demonstrate the ability of this prototype system to control pH to a specified average level over a given time period. Further discussion includes systems in-situ results analysis, corrective actions, upgrades, and the anticipated next phase for FOCE including the use of CO₂ addition to change the local chemistry. As the FOCE team continues these efforts external science communities have expressed interest in the FOCE system for their studies, such as 400 m water coral research off the coast of Norway. Just as the FACE system has extended out to work with the international community, the technology development team of FOCE is interested in addressing the questions posed by the broader oceanographic science community regarding ocean pH.

I. INTRODUCTION

Ocean CO₂ sequestration concepts and questions, and ongoing “passive” ocean acidification, are important

societal issues, and they provide interesting experimental opportunities for science researchers and the engineering staff at the Monterey Bay Aquarium Research Institute (MBARI). Debate has proliferated from the early idea proposed by Marchetti in 1977 [1] with little consideration to testing the theories about the technology and associated environmental concerns. Having easy access to the deep ocean along with teams of science and engineering at the same facility, MBARI decided to venture into small-scale in-situ experimentation and provide some insight into the questions being posed. The prevailing concepts in many sectors favor a principle that the ocean is a big place and can absorb a tremendous amount of CO₂ (Caldeira et al., 2005). The chemistry of seawater is slightly basic which makes the uptake of CO₂ from the atmosphere a natural process. The result as CO₂ is absorbed is that the ocean pH must drop. The pH cannot return until the natural weathering processes of silicate rocks dissolve and bring it back to equilibrium over time scales of 10⁴ years. The slightly basic pH value of sea water is predominant during geologic time.

At present a third of the anthropogenic CO₂ emissions are absorbed by the ocean annually, this equates to approximately 2 giga-tons of carbon (7 tons giga-tons of CO₂) per year. As the atmospheric levels of CO₂ increase the chemical disequilibrium will create a similar response in ocean absorption. Eventually the chemistry over the long duration will drive the ocean to absorb 80% to 90% of the world's atmospheric CO₂ and therefore 80-90% of anthropogenic emissions will be sequestered there. Estimates at the moment have about 500 giga-tons of anthropogenic CO₂ in the world's upper ocean waters. This is evidenced by a pH change of -0.1 in the current ocean that projections show will continue to decrease over this century another -0.2 units at least [2].

The Free Ocean CO₂ Enrichment (FOCE) experiment was created to provide a test platform for a broad spectrum of ocean science to address issues associated with anthropogenic pH change in the ocean. FOCE has been designed to create and actively control a commanded lower pH environmental condition, maintain the condition within boundary parameters, and allow in-situ multi-discipline science experiments to conduct observations and perturbations over a desired temporal scale.

II. FOCE CONCEPT

Over a number of years MBARI has performed a series of small scale CO₂ experiments. These experiments

have focused on the chemical dynamics and allowed MBARI to gain unique skills. Observation of CO_2 hydrates, and measuring reaction kinetics, has helped establish the dissolution rates and equilibration fundamentals. The same experiments have correlated amounts of CO_2 released at a central pool and the observed pH disturbances of the surrounding water. Additional studies have observed the impacts on the local biota [3]. The early experiments quickly disclosed various problems of large pH excursions driven by the tide cycles. The issues demonstrated that longer term observations would require much more stability and control over environmental manipulations such as pH and total dissolved CO_2 .

There are analogous experiments carried out on land of routine large scale CO_2 enrichments called the Free Air CO_2 Enrichment (FACE) [4]. (Fig. 1). The towers release CO_2 into the local air at controlled rates to bathe the local vegetation in anticipated levels of CO_2 that simulate the conditions for the later part of this century. Release rates are controlled using wind speed and direction. FACE sites emit various amounts of CO_2 , one specific location releases about 1,000 tons CO_2 per year.

Fig.1: A FACE (Free Air CO_2 Enrichment) experiment in Wisconsin.

The FOCE system concept is based upon the multi-year efforts and success of the FACE systems. The specifications were modified to address the environmental differences of being in the ocean such as being in an incompressible fluid, current, chemistry, mixing dynamics and closed loop control variables. The initial concept can be seen in Fig. 2. To accomplish a prototype quickly, one key decision was to use diluted hydrochloric acid (HCl) in place of CO_2 for the early experiments. Once the test concept was proven out the design allows for easily switching over to CO_2 in the future. A requirement from science was to monitor pH as the primary variable and to use the pH probe readings as the input for control. This approach presented several challenges since the dynamics of pH change is dependent on temperature, pressure, and time for either acid or CO_2 to equilibrate with the sea water. Additionally, it was recognized that a natural time delay exists in the system based on scale. Small currents or a large control area would have significant delays in reaching pH equilibrium. The delays are compounded by a need to manage the buoyancy of acid or liquid CO_2 . For the purposes of a prototype the first experiments were

Fig.2: FACE Concept as part of a cabled observatory

bounded by limiting current regimes between 10 cm/sec minimum and 30 cm/sec maximum to complete the technology demonstration. These current speeds would allow the system to have enough time to react and obtain a perceptible (though not full equilibrium) change pH within the volume of a small frame with limited amounts of HCl. Pumping a premix of fluid continuously minimizes the differential in buoyancy. Bounding the pH within an order of magnitude from previous experiments, ± 0.20 pH, gave liberal adjustment and allowed us to ignore buoyancy issues as long as the current speed stayed in the specified range. Limiting the prototype in this manner demonstrated the FOCE concept was completely feasible and scalable without substantial engineering investment.

Using the outlined approach allowed the FOCE team of science and engineering to build, integrate, tank test, and obtain results from an in situ deployment within 3 1/2 months. Power and communications were simulated by a small length of cable that tied the system to MBARI's ROV Ventana for power while using ethernet for all control and data logging functions.

III. FOCE TECHNOLOGY

The FOCE prototype design is constructed from a series of distinct subsystem components; FOCE Frame, Directional Control Valve, Mixers and plumbing, Controls, pH Instrumentation, and Additional Science Instrumentation. Each subsection was designed and built to be as simple as possible while strict interface control assured quick integration later. Each portion was developed in parallel efforts demonstrating the multi-disciplined rapid implementation program approach was easily managed with clearly defined interfaces. This also allowed the subsystem components to be independently traded against delivery, cost and schedule drivers. Compromises were often made to use what was readily at hand or could be quickly manufactured with the machine tools and equipment located within MBARI. This prevented long lead items from delaying the project and guaranteed the system would be ready by the scheduled deployment date. The additional benefit from these efforts was to demonstrate that other than a few key components requiring technical expertise the system can be designed, constructed, tested, deployed and operated by a diverse set

of science and technology individuals. This is key to the viability of the FACE concept. FACE must be configurable for a variety of science and easily transferred to the community of interested users.

A. Prototype FOCE Construction

The frame is a simple 6061 aluminum weldment with cross wire bracing. It consists of two sets of horizontal rings set 0.5 meters apart. The inner ring is 1 meter in diameter and the outer ring is 2 meters in diameter. The 0.5 meter by 1 meter diameter defines the pH control area, Fig. 3. Eight mounting points are equally spaced for perimeter pH probes. A solitary center post holds 3 pH probes separated equi-distant vertically to provide the control inputs for the system. Four vertical struts hold an upper set of rings approximately 1.5 meters from the bottom of the frame. Eight mounting points for plastic crates provide places for the HCl holding tanks. Center to the top ring is a flotation pack to set the in water

Fig. 3: FOCE Prototype in the MBARI test tank

weight. This configuration allows the prototype to be treated as an elevator system which is easily deployed and recovered using standard operational practices.

The configuration is entirely flexible which can be seen from the image in Fig 3. The tanks for fluid could easily be moved off to the side. Instrumentation is strapped on in desired locations as per science requirements. Aluminum was selected because it could easily be assembled within MBARI, but plastic structural members could easily be substituted if proper consideration was given to strength needs. The prototype has flotation at the top but this was a matter of convenience for this experiment. Because the system was intended to be deployed and recovered using one ship and ROV dive the system was designed for engineering testing and easy installation and recovery. A more permanent installation would not require flotation and could easily have nothing overhead to impede detritus, nutrient transport, current gradients, photic effects or any other environmental factor of importance to the science experiment.

B. Directional Control of pH Adjustment Media

Prototype testing implemented passive control for upstream release of the HCl and was selected to keep the electronics and equipment simple. Currently, MBARI engineering is upgrading the system design to use

solenoids for fluid release and resolvers for directional control. The first iteration was configured to use a mechanical weather vane to accomplish upstream release passively, Fig. 4. The valve is required to respond to the ambient current and direct the injected mix of acidified seawater flow to the upstream side of the FOCE frame. The vane turns an outer rotor in currents as low as 5 cm/sec and appropriately directs flow to 2 adjacent sectors on the frame out of a possible 8. A simple preliminary analysis of drag in 10-30 cm/sec seawater yielded a vane of about 250 in. sq. The valve was also constructed to near zero response to gravity or buoyancy when deployed on what most certainly would be a non-level seabed. The port seals required several trial configurations of varying interference to the rotor before a 1st article (?) was completed. During at sea trials it was demonstrated that an all mechanical valve system could function adequately. In turn, this enables a wider range of applications where power limitations could be an issue. For example, concepts being considered for moored deployments as part of the wider observatory efforts present unique challenges. Not because of the FOCE concept itself, but more due to the limitations and access of current technologies to bring adequate power readily to the bottom of the ocean. A highly simplified moored FOCE system concept can be seen in Fig 5. This image is representative of an offshore sea mount or ridgeline.

Fig. 4: FOCE Directional Control Valve

C. Plumbing

Prototyping the mechanism of pumps and tubing to deliver the HCl solution from the containers to the FOCE frame demonstrated the simplicity of the design. The acid pump head was driven by a variable speed electric motor integrated to the control electronics. Seawater was delivered to the system by an identical peristaltic pump head and motor assembly. To measure pumping rates and delivery volumes, a Hall effect turbine flow rate sensor was placed in-line subsequent to each peristaltic pump. Real-time data from these sensors was then used as feedback for controlling seawater/acid mixing ratios. The seawater and acid lines were joined at a second manifold,

Fig. 5 : FOCE Concept as a Moored System

this provided adequate mixing prior to delivering the solution in a single line to the central directional valve. The choice of soaker hose permitted a large emitter surface area and minimized system backpressure at high pumping rates. The soaker hose also promoted rapid and turbulent mixing with ambient bottom currents as can be seen in Fig 6.

Fig. 6: Soaker hose was selected for HCl release after testing a variety of methods

D. Sensors

The FOCE structure was outfitted with eleven SeaBird pH probes. Eight pH probes were fixed to the exterior 0.5 m ring with the tip of the probe approximately 25 cm from the seafloor. Data from these probes was logged internally to two CTDs. The three remaining pH probes were clustered at the center of the control volume along with a micro-CTD. The data from these sensors was relayed to the ROV control room in real time and provided the necessary pH feedback for control of the acid/seawater delivery. The system elements were modeled in a simple graphical user interface (Fig 7).

Additional instruments were also deployed and/or recorded to obtain background information which was later used to verify the prototype test results. One pH sensor was on the MBARI ROV Ventana and recorded during the entire experiment, this unit provided background pH information. An InterOcean Systems S4D current meter was placed 0.5 meters from the seafloor and approximately 5 meters away from the FOCE frame to

Fig. 7: System diagram and parameter controls page

measure current speed and direction during the duration of the two day experiment. Real time current data was provided by the ROV. This data was used to set the flow ratios on FOCE as a feed forward input in the control loop. Standard CTD data on the FOCE frame and the ROV were also collected to establish the environmental conditions for the systems test.

Fig. 8: CO2 Sniffer for Equilibrium Detection

One additional device constructed at MBARI was taken along and used to sample the waters independently from the FOCE system. A custom sensor arrangement with pumped flow called the pH sniffer was positioned at a few different spots by the ROV manipulator, Fig. 8. This device was used to sample and verify the equilibrium rates of the HCl concentrations used in the first FOCE deployment. This data was very important to determine the difference between pH equilibrated water and acidified enriched water. This data will be used to modify system parameters around environmental conditions for future FOCE deployments.

E. Modes of Operation and Software Architecture

Operation of the FOCE system is very simple using the graphical interface, Fig. 9. Due to the long time delays required to obtain equilibrium, a box car filter of first in first out values was implemented, and sampling

rates were designed into the algorithms to allow pH adjustments in fractions of hertz. This approach is beneficial since the pH sensors are sensitive and prone to appearing noisy as fluid runs past the electrodes. The filtering also uses a simple set of bounds based on the capability of the system to adjust pH. The science user can set these values in the graphical user interface (GUI). The overall ratio of fluid is adjusted by the science user inputs. Then the adjusted mix ratio of sea water to acid is automated based on the environmental current (initial experiments allowed current to be manually input for testing purposes). The delta pH from set point is then fit to a preset function, a curve that non-linearly adjusts mixing ratios as the delta pH varies further from the mean. The resultant scalar is then used to modify the acid pump rate and inversely adjust the sea water pumps rate thus maintaining a constant fluid flow into the current stream.

Fig. 9: FOCE Real Time Data Display and Control

Most system parameters can be adjusted on the top level GUI. The control software and operational diagrams were created in LabVIEW™. The approach allowed for very quick software development, immediate testing of each module and addition of features or parameters as desired by the science staff. For example, adding or deleting an additional pH sensor takes only minutes in software effort.

The integrated system and software culminate to give a desired pH value in the control volume as specified by the scientist. Referencing Figure 9 again, the desired pH level is given by the thin yellow line, the thicker yellow line is the average pH with the entire control volume. The blue, green and red lines are the three pH sensors located within the volume that are used to obtain the average. The average of the pH probes the system homes in on the selected value. The real time graph shows the filtered values of the three pH sensors being incorporated in the control loop. The analog gauge representations show the real time output values of the acid and sea water pumps. The data is collected at the selected frequency of the scientist, this is independent of the filter sample frequency. The system time is matched with the network clock used for synchronization with any

other instrumentation associated with the experiment. Time synchronization also allows for multiple FACE sites to properly correlate data sets.

IV. PERFORMANCE / RESULTS

Tank testing of the FOCE system was performed two weeks in advance of the scheduled deployment date. This allowed for fine tuning of the system and making necessary corrections to be sea worthy. A hydraulic ROV thruster was used to create an artificial current in the test tank. The system was placed at a 10 meter depth in the MBARI salt water test facility and allowed to respond as it would deployed at sea. The directional valve worked as designed, porting the acidified sea water flow to the desired up stream side of the frame. The control system also performed as desired, controlling the pumps at the levels specified and mapping to the control curve as

Fig. 10: FOCE In Situ Operations

defined by engineering. Some minor plumbing changes and tuning were performed in preparation for the field trials.

At sea testing took place on April 12th and 13th, 2005, Fig. 10. The test site selected was within the oxygen minimum zone on a fairly flat area of the Monterey Bay off the coast of central California. Records had indicated the average currents would be in the specified range and the oxygen minimum meant the pH was already low in those waters which would test the systems ability to further depress the local pH. The elevator style deployment went as planned with the system landing within meters of the desired landing site. The system was connected to the ROV using the ODI™ wet mate connector. The system was brought up and exercised with several short duration pH control experiments. The system and all sub-components worked as predicted with the pH change being controlled at +/- .03 units. Troubles were encountered when the local currents went to near zero and eventually completely slacked. The acid enriched water buoyancy issues created a pool of low pH water which was not cleared until the currents picked up again. This was not a performance issue for the FOCE prototype, as the conditions and results were known.

V. CONCLUSION / FUTURE EFFORTS

Testing to date has demonstrated the basic feasibility of moving the FACE experimentation concepts for studying enriched CO₂ conditions into the ocean.

With minimal resources and limited time a successful prototype was able to control pH within an open area of water within specified parameters as given by MBARI science staff. Further review of the data illustrated that even tighter control is possible as the design incorporates more advanced physical measurements and chemical complexities in the algorithm at the root of the systems control.

Further deployments are being planned with the prototype system to incorporate more advanced control schemes. The current system has repeatedly controlled pH within the ± 0.20 pH unit bounds. Often the system has been tested to control the pH within ± 0.10 pH units. Current designs for the deeper and less energetic environments are looking to attempt ± 0.03 pH units for the majority of a deployment. For the more energetic regions, such as closer to shore in the photic zone, designs are being traded to look at increasing residence time and reduce the amount of CO_2 or acid that would be required. Theoretically there is nothing to prevent controlling the flow through the volume under pH control within reasonable mass transfer limits. The specifications and design for controlled flow still require science review to be sure that the system can accomplish the experiments in situ without adverse impact on the data sets.

Fig. 11: FOCE Shore Based Concept

Results have shown thus far that the FOCE initial design is viable. In the context of front-line oceanography, usable results from the first time deployment are always a reason to look to the future. Now that we have met the first hurdles we have more time to work on several improvements. Among them are: a current meter for dynamic input and an electro-mechanical valve design more sensitivity to current direction low ambient flow rates. We are also considering the various configurations and applications to accomplish a series of science objectives, Fig. 11

Further testing is planned to expand the FOCE systems concepts into more challenging areas of operation. The first task is to begin addressing delivery of large amounts of CO_2 for long term testing that is required for many experiments. Other FOCE modifications for trawl resistance and interfacing with cabled or moored

observatories also need consideration. One key topic to address is bringing the system to shallower depths and more dynamic water masses, and matching these to chemical equilibration times. Theoretically, the problems are very addressable and repeatable flow could help the system reaction times. The larger issue is water masses moving past the test site, for example along-shore currents, can dominate the amount of CO_2 required. These problems are well defined in terms of the chemistry so the real issue becomes experiment funding and permitting for the necessary quantities of CO_2 . These issues are being actively pursued.

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Determination of gas bubble fractionation rates in the deep ocean by laser Raman spectroscopy

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Abstract

A new deep-sea laser Raman spectrometer (DORISS – Deep Ocean Raman In Situ Spectrometer) is used to observe the preferential dissolution of CO₂ into seawater from a CO₂-N₂ gas mixture in a set of experiments that test a proposed method of CO₂ sequestration in the deep ocean. We describe here experiments in which a 50%-50% CO₂-N₂ gas mixture is exposed to seawater at 300 m depth and the changing gas concentration is observed *in situ* with a laser Raman spectrometer. By observing the changing ratios of the CO₂ and N₂ Raman bands we are able to determine the gas flux and the mass transfer coefficient at 300 m depth and compare them to theoretical calculations for air-sea gas exchange.

In a first set of experiments performed in August 2002, an open-bottomed 10 x 10 x 10 cm cube was used to contain the gas mixture; and in a second set of experiments in October a 2.5 cm³ funnel was used to hold a bubble of the gas mixture in front of the sampling optic. Although each experiment had a different configuration, comparable results were obtained. As expected, the ratio of CO₂ to N₂ drops off at an exponential rate ($\sim e^{-0.055t}$) as CO₂ is preferentially dissolved in seawater. In fitting the data with theoretical gas flux calculations, the boundary layer thickness was determined to be ~42 μm for the gas cube, and ~165 μm for the gas funnel reflecting different boundary layer turbulence. The mass transfer coefficients for CO₂ are $k_L = 2.82 \times 10^{-5}$ m/s for the gas cube experiment, and $k_L = 7.98 \times 10^{-6}$ m/s for the gas funnel experiment.

Keywords: Instruments; Carbon Dioxide; Gas Flux; Chemical Sensor

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1. Introduction

We have carried out novel experiments to determine *in situ* the dissolution rate of gas mixtures injected into the deep ocean. Our purpose was to test under field conditions a proposal for ocean CO₂ sequestration without prior CO₂ capture (Kajishima et al., 1997; Saito et al., 2000) based upon the marked difference in solubilities of CO₂ (Aya et al., 1997; Haugan and Drange, 1992) and N₂ (Wiebe et al., 1933) gases in cold sea water at high pressure. Additionally we sought to advance the use of newly developed Raman spectrometric techniques (Brewer et al., 2004; Pasteris et al., 2004) for deep-sea geochemical studies. Laser Raman spectroscopy is useful for both chemical identification and for observations of the rate of change of gas composition with time. The dissolution behavior of gas bubbles is of fundamental interest to ocean scientists for reasons as diverse as their role in air-sea gas exchange (Keeling, 1993), to the fate of gases vented from the deep ocean floor (Massoth et al., 1989; Merewether et al., 1985; Rehder et al., 2002).

For any CO₂ sequestration procedure the cost and complexity of CO₂ capture from the combustion stream dominates the economic equation (U.S. Department of Energy, 1999). Thus, ocean injection of a N₂-CO₂ mixture at relatively shallow depth, combined with piped transfer of the dense CO₂ rich sea water formed to great ocean depth, and release of the excess N₂ gas has been proposed (Saito et al., 2000). The trade off is the increased cost of pressurization of the N₂ gas, and thus the use of an enriched CO₂ stream is preferable. For this reason, we selected a 50%-50% CO₂-N₂ gas mixture for our study. These ocean

gas injection schemes rely on a rising bubble stream to provide the surface area required for rapid dissolution. We have developed techniques for direct visual observation of rising bubble (Rehder et al., 2002) and droplet (Brewer et al., 2002b) streams in the ocean, but adopt here spectrometric analysis of a small gas volume exposed to the open ocean but held at fixed depth, temperature, and pressure for the duration of the experiment.

Raman spectrometry has seen little use as a tool by ocean scientists, but it offers the potential of rapid, non-destructive analysis of solids, liquids, and gases and recent technical developments (Brewer et al., 2004; Pasteris et al., 2004) have enabled its use in the deep sea. The complexity of the typical optical path has in the past rendered Raman most useful as a chemical identification tool rather than for quantitative analysis. However, relative concentrations of gas mixtures can readily be determined by measuring peak area ratios in the spectra, and there exists substantial opportunity for quantitative work where effective calibration protocols are possible (Sum et al., 1997; Wopenka and Pasteris, 1987). Here we take advantage of the rapidity and specificity of the Raman ratio technique and directly observe *in situ* the changing composition of a CO₂-N₂ gas mixture with time during two cruises in August and October of 2002.

2. Methods

2.1. Raman Scattering

Raman scattering is the inelastic, molecular scattering of monochromatic radiation. An incident photon exchanges energy with the target molecule and is scattered with lower or higher energy – Stokes and anti-Stokes scattering, respectively (Figure 1). The observed energy shift of the scattered radiation is equal to the change in vibrational energy of the molecule, and is not dependent on the frequency of the exciting radiation. Although both IR and Raman are types of vibrational spectroscopy, the selection rules are quite different. Whether or not a molecule is Raman-active is dependent on the polarizability of the molecule. One of the big advantages of Raman spectroscopy is that it is capable of analyzing solids, liquids, and gases. It is rapid and requires little to no sample preparation, and is (generally) non-destructive. A fuller discussion of the theory behind Raman scattering can be found in Ferraro, et al. (2003), Nakamoto (1997), and references therein.

The intensity of Raman scattering is dependent upon a number of parameters and can be written in simple form as:

$$I_R = (I_L \sigma \eta) P \cdot C \quad (1)$$

where I_R is the measured Raman intensity, I_L is the laser intensity, σ is the Raman cross-section or efficiency, η includes instrument parameters such as optical transmission and collection efficiency, P is the sample path length, and C is the concentration (Pelletier, 1999). The Raman cross-section differs for

different molecules and different phases. Additionally, Raman intensity is affected by the optical path; therefore peak heights or areas cannot necessarily be compared directly from one measurement to the next. However, peak ratio techniques, which are independent of optical path, exposure time, and other experimental factors, may be used to determine relative concentrations.

We use the ratio method of Wopenka & Pasteris (1987) in a manner similar to Sum et al. (1997) for a two-component system to obtain an expression relating the concentration C_i of species A and B to the measured Raman band areas (A_i), Raman cross sections (σ_i), and the instrumental factors (η_i) by

$$\frac{C_A}{C_B} = \frac{A_A}{A_B} \frac{\sigma_B}{\sigma_A} \frac{\eta_B}{\eta_A} = \frac{A_A}{A_B} \times \frac{F_B}{F_A} \quad (2)$$

where F_i is defined as the “Raman quantification factor.” This yields an expression similar to Beer’s Law, widely used in spectrophotometric procedures. In a similar manner, since the fundamental measurement of the molar absorptivities etc. is difficult, Beer’s Law is usually applied by constructing a calibration curve. In this case the practical protocols for *in situ* calibration are still evolving, and we use here a single internal reference standard. Sum et al. (1997) have shown that CH₄-CO₂ gas mixtures measured by Raman spectroscopy have a linear calibration curve, and thus although it was not possible to introduce a number of contained known gas mixtures to the probe to provide a direct gas based calibration, we assume that the less complex N₂-CO₂ mixture also yields a linear response.

2.2. Instrumentation

Direct measurements of the CO₂-N₂ gas ratio were obtained with MBARI's *in situ* laser Raman spectrometer system called DORISS (Deep Ocean Raman In Situ Spectrometer). This sea-going instrument is based on a laboratory model laser Raman spectrometer (LRS) from Kaiser Optical Systems and consists of a 532 nm Nd:YAG laser, a holographically filtered probe head, a holographic duplex grating, and a 512x2048 front illuminated CCD camera from Andor Technology. The spectral range of DORISS is 100-4400 Δcm^{-1} . The duplex grating splits the spectrum into two stripes on the face of the CCD chip providing a mapping of $\sim 1 \text{ cm}^{-1}$ per pixel. The resolution at the time of the deployment was $\sim 7 \text{ cm}^{-1}$.

The instrument is packaged in three pressure housings connected by copper and fiber optic cables for use in the ocean to depths as great as 4000 m (Brewer et al., 2004). The immersion sampling optic used for this experiment has an f/2 lens at the end of a 10 inch-long metal tube with a sapphire window rated to 3000 psi. The working distance of the immersion optic is 4 mm in air, 7 mm in water. The spectrometer was calibrated in the lab prior to deployment. A neon source was used for wavelength calibration and a calibrated tungsten lamp was used for intensity calibration. The laser wavelength was checked by looking at the position of the 801 Δcm^{-1} Raman line of cyclohexane (Tedesco and Davis, 1999). The wavelength calibration of the spectrometer can be affected by changes in temperature (DORISS experienced a temperature drop of $\sim 7^\circ\text{C}$ during the deployment). Therefore, a diamond plate was placed in the beam path of the

laser inside the probe head as a reference standard (Brewer et al., 2004; Zheng et al., 2001). The 1332 cm^{-1} diamond Raman line is thus superimposed on all collected spectra as a calibration check.

During the time of the deployments discussed here, the instrument was still under development and some components were changed. These components include an X-Y-Z stage (referred to as a laser injector) used to couple the laser to the $62.5\text{ }\mu\text{m}$ excitation fiber. The injector provided by the vendor was replaced by a more robust custom built injector which assured higher laser power output and greater stability. Additionally, the slit alignment mechanism in the spectrometer was replaced with a motorized stage. The original slit alignment mechanism was designed to be operated manually with a thumb wheel. Thus, when the spectrometer was sealed in its pressure housing, the slit could not be aligned. Before the motorized stage was installed, no slit was used. Thus the effective slit width was $100\text{ }\mu\text{m}$ (the size of the collection fiber). After the motorized stage was installed, a $50\text{ }\mu\text{m}$ slit was used. Lastly, the diamond chip in the probe head was repositioned between deployments to reduce extraneous scattering off the edges of the chip.

An important characteristic of a new instrument is its detection limit. During the development of the DORISS instrument, changes in configuration have caused changes in sensitivity (and hence detection limit) from one experiment to another. However, based on our August data, we can make some assumptions regarding the detection limit of the instrument. It should be noted that this is most likely a conservative estimate as improvements to the system

which increase sensitivity and decrease noise are currently being implemented. Additionally, the detection limit is dependent upon the Raman efficiency of the target which varies from one molecule to another. Table 1 shows the signal to noise ratio for the CO₂ and N₂ bands from the August data. The duplex grating used in the spectrometer, divides the spectral region into two stripes – a “high lambda” stripe ($\sim 0\text{-}2400\text{ }\Delta\text{cm}^{-1}$) and a “low lambda” stripe ($\sim 2200\text{-}4400\text{ }\Delta\text{cm}^{-1}$). The N₂ band is observed on the “high lambda” stripe which has less noise. Assuming that a signal-to-noise ratio of 3 is required, DORISS is capable of detecting concentrations as low as 2.4 mol% for CO₂ and 2.3 mol% for N₂ in this configuration.

Table 1

Estimates of DORISS detection limits for gaseous CO₂ and N₂ at 30.86 atm

	Band area (counts)	RMS Noise	Signal-to- Noise	Limit of Detection (S/N = 3)	Limit of Quantification (S/N = 10)
CO₂					
	2917	47	~ 60	2.4 mol%	8.1 mol%
N₂					
	1965	30	~ 65	2.3 mol%	7.6 mol%

2.3. Raman spectra analysis

The spectral data were analyzed using GRAMS/AI data processing software (from ThermoGalactic). Nitrogen has a single Raman peak at $2332\text{ }\Delta\text{cm}^{-1}$. Carbon dioxide is characterized by the Fermi diad: peaks at $\sim 1285\text{ }\Delta\text{cm}^{-1}$ from the bending mode ($2\nu_2$) and at $\sim 1388\text{ }\Delta\text{cm}^{-1}$ from the symmetric stretch mode (ν_1). The peak position (i.e., Raman shift), height and area were determined

using the GRAMS/AI peak fitting routine. When identifying peaks, the same wavenumber regions were analyzed for all spectra, and baseline values were determined by the peak fitting routine for those regions. As noted above, since Raman intensity is affected by the optical path, peak areas cannot be compared directly from one experiment to the next (i.e., data from the August experiment cannot be directly compared to the October experiment due to changes in the optical path and configuration of the instrument). Therefore, we examined ratios of the CO₂ to N₂ peak areas which are independent of exposure time, optical path, and instrument configuration.

3. Field Experiments

DORISS was deployed in Monterey Bay using MBARI's remotely operated vehicle (ROV) Ventana (Figure 2). The ROV Ventana provides power and communications to DORISS, and is controlled by pilots and scientists aboard the support ship, the R/V Point Lobos, through a ~2 km-long tether. Measurements of the gas mixture were made at depths of 100-400 m (well above the seafloor at that location). The ROV's external HID lights were turned off during acquisition of spectra. These lights produce strong peaks across the spectral region of the DORISS instrument.

This paper will focus on data collected at 300 m during two dive series. The ambient seawater temperature at that depth was 7.9°C, and the pressure was ~300 dbar. At this temperature and pressure pure CO₂ is a gas and is clearly outside of the hydrate stability field (Figure 3a). However, for this experiment we used a 50-50 (mole %) mixture of CO₂ and nitrogen; for this mixture the

phase boundaries are dramatically shifted due to CO₂-N₂ interactions. A liquid phase will not form under any PT conditions encountered in Monterey Bay, nor will CO₂ clathrate hydrate form under the conditions of the experiment (Figure 3b); we calculated the physical properties using MultiFlash 3.2 (Infochem, Inc., London).

A 50-50 (mole %) mixture of carbon dioxide and nitrogen was prepared by first filling an evacuated SCUBA tank to 800 psia with commercial grade CO₂ at ambient temperature (21.9°C) and then filling with UHP nitrogen gas to 1600 psia. This second step was done in two parts by allowing the cylinder to cool to ambient temperature overnight between fillings. We estimate that the composition is within $\pm 5\%$ of the target mixture based upon uncertainties in the pressure and temperature at time of filling. The SCUBA tank was allowed to sit to achieve complete mixing of the gases for 40 hours before use. The same gas mixture was used for both the August and October deployments.

3.1. August 2002 experiments

A preliminary set of measurements was obtained in August 2002. The laser power exiting the probe tip was measured to be ~ 10 mW on deck prior to the dive. During this experiment, the immersion optic was inserted into a hole in the side of an open-bottomed 10x10x10 cm cube; thus the optic tip was in a pocket of gas and no seawater was in the beam path (Figure 4). The gas cube was filled with a 50%-50% CO₂-N₂ gas mixture from a port at the top of the box; thus, very little mixing with seawater occurred during filling. A second valve allowed the box to vent gas upwards while filling with seawater through

the open bottom. With this configuration we were easily able to collect quality spectra of a 50%-50% mixture of CO₂ and N₂ gas and 100% N₂ gas. Two sets of measurements were collected at 300 m depth – a series of 10 x 10 sec accumulations spanning 23 minutes, and a series of 5 x 5 sec accumulations spanning 16 minutes. The box was purged and refilled with gas before each experiment.

Different targets have different Raman scattering efficiencies, thus raw peak heights cannot be used to determine relative concentrations. The gas cube experiment provided a baseline to understand the relative intensities of the Raman signals from CO₂ and N₂. We were also able to observe the preferential dissolution of CO₂ into seawater. However, due to the low ratio of the seawater-exposed area to the gas volume ($\sim 0.1 \text{ cm}^{-1}$) we were not able to observe the complete diffusion of CO₂ from the gas cube during the time of our experiment (~ 30 minutes).

3.2. October 2002 experiments

In October of 2002 we performed another series of experiments to observe the preferential dissolution of CO₂ from a 50%-50% CO₂-N₂ gas mixture. Based upon the results from our August cruise we were able to scale the experiment appropriately, such that complete CO₂ dissolution could be observed in ~ 30 minutes. In this experiment we attempted to mimic the bubble experiments of Brewer, et al. (2002b). The probe head was positioned in a downward-looking orientation and a clear conical funnel was placed on the tip of the immersion optic to hold a buoyant gas bubble in the DORISS beam path (Figure 5). The

total volume of the funnel was 2.5 cm^3 , and the ratio of the exposed area to the gas volume was increased 20-fold from the earlier gas cube experiment. The laser power for this experiment was measured to be $\sim 13 \text{ mW}$ prior to the dive.

Two experiments were run with the funnel configuration, both at a depth of 300 m, with spectra being collected every 5 minutes over a 30 minute period. During the first run, each spectrum was an average of 10 accumulations of 10 second exposures. Thus, each spectrum was an average over a time span of 100 seconds. During the second run, each spectrum was an average of fifteen 15-second exposures (time span of 225 seconds). The funnel was thoroughly flushed with the gas mixture prior to each experiment.

4. Results

4.1. *August 2002 data*

The data from the August dives provide information on the relative Raman scattering efficiencies of nitrogen and carbon dioxide. Initial spectra from both experiments are shown in Figure 6. The two CO_2 peaks (~ 1285 and $\sim 1388 \text{ cm}^{-1}$) are separated by the diamond reference peak (1332 cm^{-1}) in the left half of the spectrum; the N_2 peak (2332 cm^{-1}) is on the right half of the spectrum. The dropout at 1942 cm^{-1} is due to a flaw on the CCD chip. We compared the area ratios of both CO_2 bands to the N_2 band to examine any differences in the Raman efficiencies. Immediately after the cube was filled, the ratio of the CO_2 bend band ($\sim 1285 \text{ cm}^{-1}$) to N_2 was ~ 1.1 ; the ratio of the CO_2 stretch band ($\sim 1388 \text{ cm}^{-1}$) to N_2 was ~ 1.9 . These ratios were the same for both sets of

measurements – 10 x 10 sec exposures and 5 x 5 sec exposures. The peak area ratios observed over time (Figure 7) show the decrease in CO₂ relative to N₂ in the gas mixture. The 5 x 5 sec accumulations show more scatter in the data than the 10 x 10 sec accumulations as expected due to higher noise levels in shorter exposures.

4.2. *October 2002 data*

The data from the October dives provide information on the rate at which CO₂ is preferentially dissolved into seawater. Two sets of measurements were made with the small funnel configuration (Figure 5) – a series of 10 x 10 sec accumulations and a series of 15 x 15 sec accumulations each spanning ~30 minutes. It should be noted that in the raw data the diamond peak area is approximately the same in the October data as it is in the August data. However, the peak areas of the gas components are ~2.5 times as strong in the August data as they are in the October data. This is due to the changes in the instrument between cruises and differences in the optical path for the two experiments (i.e., the large gas cube used in August versus the small gas funnel used in October). Despite the fact that the absolute peak area values are different, the peak area ratios are not affected and can be compared.

The October data show starting ratios of ~1.5 for the CO₂ stretch band to N₂, and ~0.8 for the CO₂ bend band to N₂. These numbers are slightly lower than those observed from the August dives (~1.9 and ~1.1, respectively). This is likely due to the fact that a) the gas is bubbled up into the funnel through seawater allowing some gas dissolution, and b) the scaling of the experiment

leads to faster dissolution of CO₂ as compared to the gas cube experiment. Thus, some CO₂ dissolution has already occurred before (or while) the initial spectra are being obtained. Calculations and comparisons with the August data suggest that the starting ratio for the October experiments is actually ~44%-56% CO₂-N₂.

During the October experiments, the complete dissolution of CO₂ can be observed within ~30 minutes. Spectra were collected every five minutes during this time and show the decreasing CO₂ Raman peaks (Figure 8). The CO₂ peaks were much smaller in the October measurements than they were in the August measurements (Figure 6) with respect to the diamond peak. By plotting the ratios over time we can fit an exponential curve to the data (Figure 9, Table 2). The exponential drop off of the data is due to the fact that since CO₂ is preferentially dissolved, the mole fraction of CO₂ in the gas mixture decreases over time which leads to a slowing of the dissolution rate.

Table 2

Curve Fits for October 2002 data

Area Ratios	Least Squares Fit	R ²
<i>Experiment 1 – 10 x 10 sec</i>		
CO ₂ stretch / N ₂	$1.5984 e^{-0.0587 x}$	0.9885
CO ₂ bend / N ₂	$0.8646 e^{-0.0583 x}$	0.9697
<i>Experiment 2 – 15 x 15 sec</i>		
CO ₂ stretch / N ₂	$1.4411 e^{-0.0536 x}$	0.9466
CO ₂ bend / N ₂	$0.7242 e^{-0.0532 x}$	0.9039

5. Discussion

5.1. *Air-sea gas exchange*

The mechanism of gas exchange across an air-water interface has been studied for years in order to better understand ocean interaction with the overlying atmosphere which has implications for global climate. Researchers typically use two-layer models where thin boundary layers are present in both the gas phase and the liquid phase (e.g., Liss and Slater, 1974), or single-layer stagnant boundary layer models where a gradient exists only in the water layer (e.g., Broecker and Peng, 1974). These models assume that both the air and water layers are well mixed while gradients exist only in thin films at the interface.

Our gas dissolution experiments provide a small-scale look at gas transfer across a gas-liquid interface at high pressure, and absent turbulent wind forcing of either the gas or water components; only local ocean water velocities perturb the interface. We assume that both the gas volume and the seawater below it are well mixed, however we do not have knowledge of the diffusive boundary layer thickness. Our initially 50%-50% CO₂-N₂ gas mixture changes composition with time and decreases in total volume as gas is transferred to the seawater below. We will use typical values for the stagnant boundary layer model to calculate expected fluxes and concentrations and compare them to the data collected with the DORISS system.

The gas exchange rate of CO₂ presents a special case due to the complex chemistry involved (Zeebe and Wolf-Gladrow, 2001). Typically it is the much

slower rate of atmosphere-ocean CO₂ gas exchange that engages the attention of ocean chemists. Bolin (1960) first drew attention to this, and the phenomenon is due to the buffer capacity of seawater and the relatively long time scales to achieve chemical equilibrium within the aqueous CO₂ system. The net result is a gas exchange rate for CO₂ $\cong$ 10x slower than for typical atmospheric gases, including nitrogen, thus it may be disconcerting to see the discussion here of the rapid exchange of CO₂. This arises from the extraordinary increase in solubility of CO₂ in seawater with pressure (Aya et al., 1997; Haugan and Drange, 1992; Rehder et al., 2004) until the hydrate phase boundary is reached. The effect of pressure on the diffusion coefficients in both the gas and liquid phases is small, and the rate changes compared to 1 atmosphere that we see are driven almost entirely by the solubility function.

5.2. *Theoretical calculations*

Since we may neglect the complexities of the ocean-atmosphere boundary layer, we may use a simple rendition of the gas exchange equation. From Henry's Law the amount of gas dissolved in a volume of solvent (C_l) is proportional to the partial pressure of the gas (P_g) in the gas volume (atm) in equilibrium with the solution, and the ratio can be described by a solubility constant, K (mol/L/atm).

$$C_l = K \cdot P_g \quad (3)$$

Using the stagnant film model (Broecker and Peng, 1974; Broecker and Peng, 1982), the flux of gas across the interface can be calculated by

$$F = D \cdot \frac{C_{top} - C_{bottom}}{z} \quad (4)$$

where F is the gas flux (mol/cm²/s), D is the coefficient of molecular diffusion (cm²/s), C_{top} and C_{bottom} are the concentrations at the top and the bottom of the boundary layer (mol/L), and z is the thickness of the boundary layer. The bottom of the boundary layer is in equilibrium with the seawater below (C_{sw}) and the top of the boundary layer is in equilibrium with the gas layer above (Equation 3). Therefore, Equation 4 can be rewritten as

$$F = D \cdot \frac{K \cdot P_g - C_{sw}}{z} \quad (5)$$

Values for the equilibrium concentration in seawater, diffusion coefficient, and solubility of CO₂ and N₂ are given in Table 3a for the surface ocean at 1 atm and in Table 3b for a depth of 300 m and 30.86 atm pressure. Literature values for the boundary layer thickness obtained from laboratory experiments vary from ~10 to ~300 μm, while radiocarbon calculations suggest an average ocean boundary layer thickness of ~40 μm (Broecker and Peng, 1974).

At the beginning of the experiment, the partial pressures of CO₂ and N₂ in the gas volume are the same (15.43 atm). The values for the equilibrium concentration in seawater, diffusion coefficient, and solubility of CO₂ and N₂ in at 300 m depth are given in Table 3b. Equation 3 shows that for both CO₂ and N₂, the dissolved gas concentration in equilibrium with the gas phase is higher than the gas concentration in seawater. Therefore, both gases should dissolve into seawater over time. Using Equation 5 and assuming a boundary layer

thickness of 40 μm , we find that the flux of CO_2 into seawater (1.27×10^{-6} $\text{mol}/\text{cm}^2/\text{s}$) is much higher than that of N_2 (4.45×10^{-8} $\text{mol}/\text{cm}^2/\text{s}$) due to its higher solubility. Therefore, the concentration of N_2 in the gas phase should increase over time as CO_2 is preferentially dissolved.

Table 3a**Gas properties for CO_2 and N_2 in the surface ocean (1 atm)**

	CO_2	N_2
Gas concentration in seawater, C_{sw} (mol/L) ^a	2.00×10^{-5}	6.20×10^{-4}
Diffusion coefficient, D (cm^2/s) @ 8°C ^b	1.17×10^{-5}	1.21×10^{-5}
Solubility, K (mol/L/atm) @ 8°C ^c	47.2×10^{-3}	6.46×10^{-4}

^a From Broecker & Peng (1982).

^b Interpolated from Broecker & Peng (1974).

^c From Weiss (1970).

Table 3b**Gas properties for CO_2 and N_2 at 300 m depth (30.86 atm)**

	CO_2	N_2
Gas concentration in seawater, C_{sw} (mol/kg) ^{a,b}	4.90×10^{-5}	5.36×10^{-4}
Diffusion coefficient, D (cm^2/s) @ 8°C ^c	1.17×10^{-5}	1.21×10^{-5}
Solubility, K (mol/kg/atm) @ 8°C ^d	2.80×10^{-2}	9.89×10^{-4}

^a From CO2sys version 01.05 (Lewis, BNL).

^b From Weiss (1970).

^c Interpolated from Broecker & Peng (1974); Note that diffusion coefficient is not significantly affected by pressure.

^d Calculated using MultiFlash 3.2 (Infochem Inc., London).

5.3. *Comparison with Raman measurements*

From Equation 2, we see that the area ratio of the CO₂ and N₂ Raman bands is proportional to the ratio of their concentrations. We know the initial concentration of the gases in the gas mixture, which provides us with a calibration point. We can then determine the concentration ratio of the gas mixture over time from the ratio of the Raman peak areas. The mole fractions are determined from the concentration ratios over time and can be compared to theoretical calculations based on the gas flux equation (Equation 5) above.

We first looked at the 10 x 10 sec data from the August 2002 experiment using the 10x10x10 cm gas cube. The cube shape maintains a constant exposed surface area (100 cm²) as the gas volume decreases. The signal-to-noise ratio of the instrument appears to have been higher by a factor of 5 during this deployment compared to the October deployment. Additionally, the slow rate of dissolution is a good match for the long exposure times (i.e., 10 x 10 sec accumulations, 100 sec total exposure time). The observed data is shown in Table 4. The peak areas of the CO₂ bands (stretching band: ~1388 Δcm^{-1} ; bending band: ~1285 Δcm^{-1}) decrease over time corresponding to a decrease in mole fraction and concentration. The peak area of the N₂ peak (~2332 Δcm^{-1}) increases over time, corresponding to an increase in mole fraction and concentration. Concentration ratios are calculated from the ratios of both CO₂ bands to nitrogen. As expected, the concentration ratios determined from each CO₂ band are quite similar. The mean value of the concentration ratio is used to

determine the mole fractions of CO₂ and N₂. The density of the gas mixture is calculated using MultiFlash 3.2 from the mole fractions.

Table 5 shows calculated values for moles, mole fraction, partial pressure and gas flux over time. This data is based on the initial conditions (shown in the first row of Table 4) and flux calculations discussed in the previous section. While a boundary layer thickness (z) of 40 μm was assumed in the previous section, a value of $\sim 42 \mu\text{m}$ is needed to approximate the observed data. As expected the gas flux of CO₂ is much higher than that of N₂ (by a factor of almost 30). As the CO₂ is preferentially dissolved into seawater its mole fraction and flux decrease over time. This slowing of the flux causes the observed exponential drop-off of the data (Figure 9). Based on the calculations, the change in volume of the gas over 1200 sec is 89.88 cm³. By looking at video frame grabs of the experiment, we observed that the gas volume has decreased by approximately 1 cm in height which is $\sim 100 \text{ cm}^3$ in volume.

The same observational to theoretical comparison can be made for the October data from the 2.5 cm³ gas funnel. Due to the shape of the funnel, the surface area exposed to seawater decreases over time as the gas volume decreases. Table 6 shows the observed data from the 10x10 second experiments. As noted in section 4.3, the starting gas mixture appears to be 44%-56% CO₂-N₂. The calculated values of moles, mole fraction, partial pressure, and gas flux are shown in Table 7. Unlike the calculations for the August data, a boundary layer thickness of $\sim 165 \mu\text{m}$ is necessary to approximate the data from the October experiment, possibly due to reduced boundary layer turbulence within

the small gas funnel. The rate of change in gas composition in the October experiment is also higher (by as much as an order of magnitude) than those in the August experiment. This is due to the higher seawater-exposed area to gas volume ratio as noted in section 3.2.

A comparison of the observed and theoretical data from the August and October experiments is shown in Figure 10. Due to the volume/exposed surface area scaling of the experiment, the proportion of CO₂ loss occurs more rapidly in the October experiment. In both cases, the theoretical calculations match quite well to the observed data. The August data shows a slight curvature that is not matched by the theoretical line. This may be due to the fact that as the gas volume in the cube decreases an enriched liquid layer is confined in the lower portion of the cube which slows the dissolution rate over time.

Table 4**Observation of CO₂ and N₂ dissolution from the 10x10x10 gas cube (August 2002, 10x10 sec data)**

Elapsed Time	Observed Peak Area (counts)			Observed Concentration Ratios		Mean Conc. Ratio	Mean Observed Mole Fraction		Mean Density
(minutes)	CO ₂ -bend	CO ₂ -stretch	N ₂	CO ₂ -bend / N ₂	CO ₂ -stretch / N ₂	CO ₂ /N ₂	CO ₂	N ₂	(g/cm ³)
2.835	6570.18	11509.87	5970.24	1.0000	1.0000	1.0000	0.5000	0.5000	0.05247
7.835	6244.39	10618.65	6217.04	0.9127	0.8859	0.8993	0.4735	0.5265	0.05156
12.835	6413.19	11028.22	6650.53	0.8763	0.8601	0.8682	0.4647	0.5353	0.05127
17.835	6354.80	10961.24	6888.00	0.8383	0.8254	0.8319	0.4541	0.5459	0.05091
22.835	6151.88	10293.63	6713.86	0.8326	0.7953	0.8140	0.4487	0.5513	0.05074

Table 5**Theoretical calculation for the 10x10x10 gas cube**

Elapsed Time	Calculated Moles in Gas Cube (moles)			Calculated Mole Fractions		Calculated Partial Pressure (atm)		Calculated Gas Flux (mol/cm ² /sec)	
(minutes)	CO ₂	N ₂	Total	CO ₂	N ₂	CO ₂	N ₂	CO ₂	N ₂
2.835	0.7252	0.7252	1.4505	0.5000	0.5000	15.43	15.43	1.22E-06	4.29E-08
7.835	0.6890	0.7239	1.4130	0.4876	0.5124	15.05	15.81	1.19E-06	4.40E-08
12.835	0.6537	0.7226	1.3763	0.4750	0.5250	14.66	16.20	1.16E-06	4.52E-08
17.835	0.6193	0.7212	1.3406	0.4620	0.5380	14.26	16.60	1.13E-06	4.63E-08
22.835	0.5859	0.7198	1.3058	0.4487	0.5513	13.85	17.01	1.09E-06	4.75E-08

Table 6**Observation of CO₂ and N₂ dissolution from the 2.5 cm³ gas funnel (October 2002, 10x10 sec data)**

Elapsed Time	Observed Peak Area (counts)			Observed Concentration Ratios		Mean Conc. Ratio	Mean Observed Mole Fraction		Mean Density
(minutes)	CO ₂ -bend	CO ₂ -stretch	N ₂	CO ₂ -bend / N ₂	CO ₂ -stretch / N ₂	CO ₂ /N ₂	CO ₂	N ₂	(g/cm ³)
0.835	1470.19	2917.10	1965.93	0.6795	1.0000	0.8398	0.4565	0.5435	0.05099
5.835	1382.26	2330.03	1965.12	0.6392	0.6150	0.6271	0.3854	0.6146	0.04870
10.835	1033.23	2007.34	2091.80	0.4488	0.4978	0.4733	0.3213	0.6787	0.04672
15.835	924.62	1498.20	2278.50	0.3687	0.3411	0.3549	0.2619	0.7381	0.04497
20.835	602.14	1258.03	2393.78	0.2286	0.2726	0.2506	0.2004	0.7996	0.04321
25.835	578.26	998.37	2560.65	0.2052	0.2022	0.2037	0.1692	0.8308	0.04234
31.665	321.32	601.52	2546.84	0.1146	0.1225	0.1186	0.1060	0.8940	0.04062

Table 7**Theoretical calculation for the 2.5 cm³ gas funnel**

Elapsed Time (minutes)	Calculated Moles in Gas Cube (moles)			Calculated Mole Fractions		Calculated Partial Pressure (atm)		Calculated Gas Flux (mol/cm ² /sec)	
	CO ₂	N ₂	Total	CO ₂	N ₂	CO ₂	N ₂	CO ₂	N ₂
0.835	0.001648	0.111962	0.003610	0.4565	0.5435	14.09	16.77	3.15E-07	1.32E-08
5.835	0.001242	0.001943	0.003185	0.3899	0.6101	12.03	18.83	2.69E-07	1.49E-08
10.835	0.000918	0.001923	0.002841	0.3231	0.6769	9.97	20.89	2.23E-07	1.66E-08
15.835	0.000666	0.001902	0.002568	0.2594	0.7406	8.01	22.85	1.79E-07	1.82E-08
20.835	0.000475	0.001880	0.002355	0.2017	0.7983	6.23	24.63	1.39E-07	1.97E-08
25.835	0.000333	0.001857	0.002190	0.1522	0.8478	4.70	26.16	1.05E-07	2.09E-08
31.665	0.000217	0.001830	0.002046	0.1060	0.8940	3.27	27.59	7.31E-08	2.21E-08

6. Conclusions

Laser Raman spectroscopy is a useful and valuable tool for performing *in situ* analysis in the deep ocean. Changing processes can be observed in real-time, and both qualitative and quantitative data can be obtained. This capability will enhance many CO₂ and gas hydrate studies (e.g., Brewer et al., 2002a; Brewer et al., 2002b; Rehder et al., 2002; Rehder et al., 2004), and can be extended to a very wide range of ocean science, including hydrothermal vent studies.

Saito et al. (2000) have proposed a method for CO₂ sequestration that employs a gas-lift pump (GLAD – Gas Lift Advanced Dissolution) system and would be effective for low-purity CO₂. From laboratory experiments at atmospheric pressure, they have determined the mass transfer coefficients (k_L) for pure CO₂ and a mix of 95% CO₂ and 5% air (Saito et al., 1999). The average mass transfer coefficient for CO₂ is 2.0×10^{-4} m/s, and that of the low purity CO₂ is slightly less. Our work performed at a depth of 300 m (the depth proposed for gas injection in the GLAD system) using a 50%-50% CO₂-N₂ mixture shows a lower CO₂ mass transfer coefficient: $k_L = 7.98 \times 10^{-6}$ m/s for the gas funnel experiment. Saito (1999) showed that the mass transfer coefficient is lower for lower purity CO₂, and this is supported by our lower numbers for a 50% CO₂ gas mixture. However, one would expect the mass transfer coefficient to be higher at higher pressure. This is not supported by our work. It should be noted that our work is for a stationary bubble held at a fixed depth, while Saito's work refers to a rising bubble stream. Additionally, our

estimates assume a seawater phase undersaturated with respect to CO₂, and in a large scale system the surrounding seawater would approach saturation and the gas dissolution rate would slow down.

Our observations support the initial very rapid loss of CO₂ from the gas phase to the liquid phase, but the time scale for complete dissolution of CO₂ is quite long. One-centimeter diameter gas bubbles, ascending at a rate of ~25 cm/sec, would transit approximately 450 m of ocean water column before being stripped of essentially all their CO₂. This casts doubt on the feasibility of the gas-lift scheme unless very small diameter bubbles can be created.

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Figures

Figure 1. Raman scattering is the inelastic scattering of monochromatic radiation. An incident photon exchanges energy with the target molecule and is scattered with lower (Stokes) or higher (Anti-Stokes) energy than the incident energy.

Figure 2. The DORISS instrument on the ROV Ventana. The spectrometer housing and electronics housings are mounted in a drawer in the ROV toolsled (shown by arrow). The probe head is carried in front (left in the picture below) for deployment by the ROV manipulator.

Figure 3. Phase diagram for pure CO₂ in seawater (A) and 50%-50% CO₂-N₂ mixture in seawater (B) calculated using MultiFlash 3.2 (Infochem, Inc., London). The grey regions indicate the hydrate stability zones, the dash-dotted line indicates the liquid gas boundary. The red line is a temperature profile from Monterey Bay, and the X indicates the experimental conditions of our deployments.

Figure 4. A video frame grab showing the DORISS probe tip penetrating the open-bottomed gas cub (10 x 10 x 10 cm). The ports at the top of the cube are used to fill and vent the cube. (From Brewer et al., 2004)

Figure 5. a) A frame grab showing the DORISS probe tip with gas funnel and gas dispensing tub. b) A cross-section of the experimental set up.

Figure 6. Raman spectra of 50%-50% CO₂-N₂ gas mixture in gas cube during August 2002 dives. The diamond reference peak is at 1332 Δcm^{-1} . The two CO₂ peaks are at 1285 Δcm^{-1} (bending mode) and 1388 Δcm^{-1} (stretching mode). The N₂ peak is at 2332 Δcm^{-1} . The drop out at ~ 1900 Δcm^{-1} is due to a flaw on the CCD chip.

Figure 7. Peak area ratios over time from the August 2002 gas cube experiment. Data points are plotted at the midpoint of the accumulation time.

Figure 8. Raman spectra of CO₂ over time. Each spectrum is an average of fifteen 15-second exposures (3.75 minute average). The diamond reference peak is at 1332 Δcm^{-1} . The two CO₂ peaks are at 1285 Δcm^{-1} and 1388 Δcm^{-1} and decrease over time as CO₂ is dissolved into seawater. The N₂ peak is at 2332 Δcm^{-1} and is not shown in this segment of the spectra.

Figure 9. Peak area ratios over time for the October 2002 gas funnel experiments. Spectra from experiment 1 are averages of ten 10-second exposures (1.67 minute averages). Spectra from experiment 2 are averages of fifteen 15-second exposures (3.75 minute averages). The decrease in the ratios of the peak areas of the CO₂ bands to N₂ band can be fit by an exponential curve. Data points are plotted at the midpoint of the accumulation time.

Figure 10. Observed and calculated CO₂ mole fraction from August and October deployments. The symbols indicate the observed values, the lines indicate the mole fraction calculated using the gas flux equation.