Experiments on Ocean CO2 Sequestration

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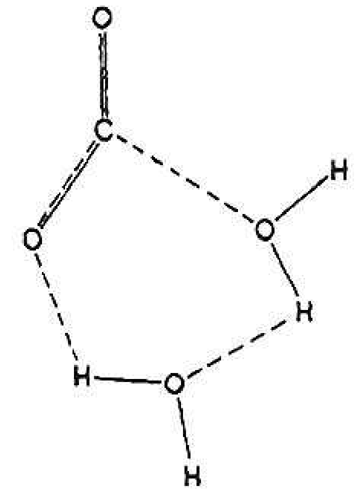


Figure 5. Possible transition state involving more than one water molecule.

Symposium "Klima und Energie"
Deutschen Physikalischen Gesellschaft
4-9 Marz, 2005

Acknowledgements

My colleagues:

Edward Peltzer, Peter Walz – MBARI
Izuo Aya, Kenji Yamane, Ryuji Kojima – NMRI, Osaka
Noriko Nakayama – ORI, Tokyo
Peter Haugan – U. Bergen

The pilots of the ROVs Ventana and Tiburon

Support from:

The David and Lucile Packard Foundation
The US Dept. of Energy
New Energy and Industrial Technology Organization (NEDO), Japan

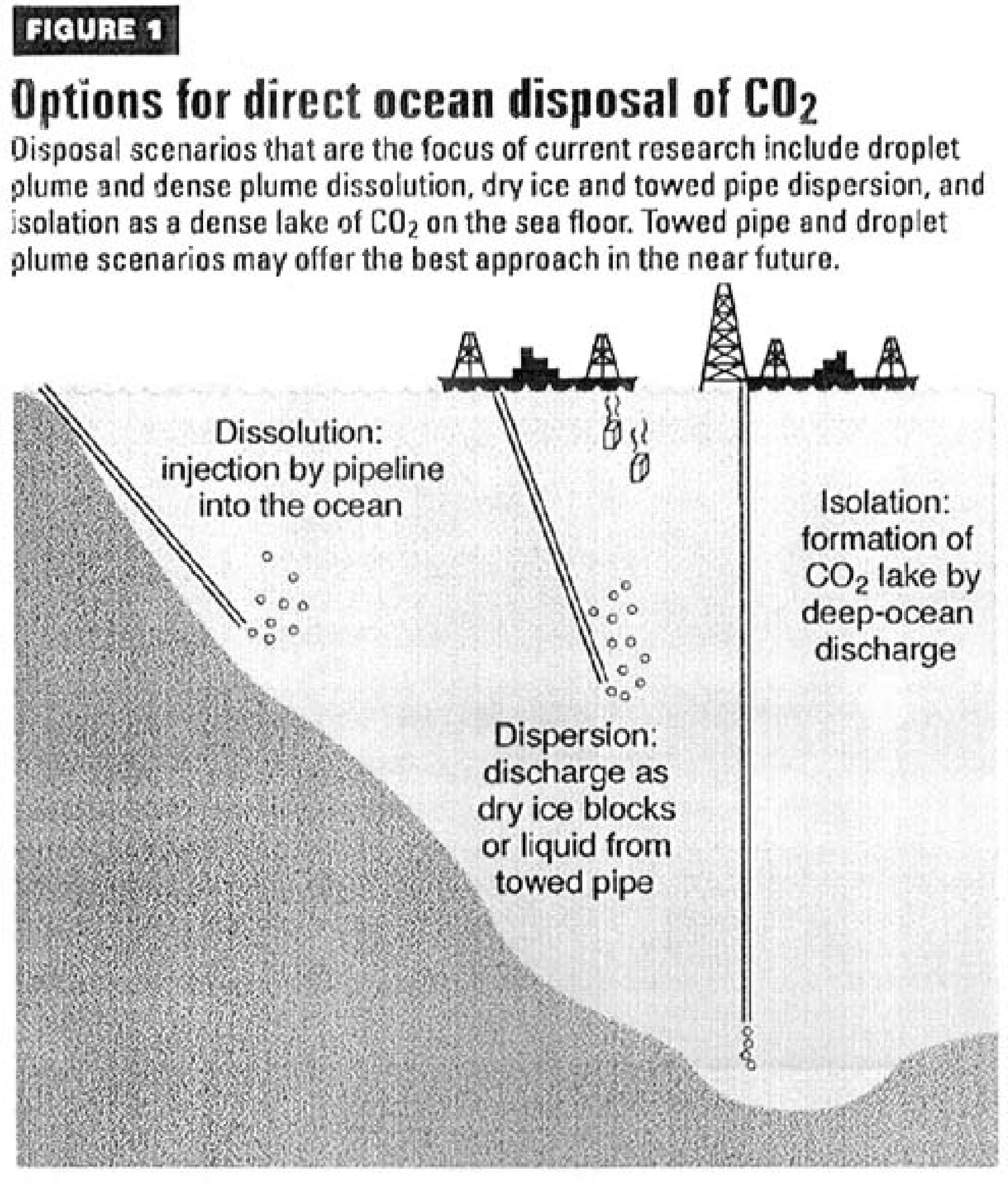


FIGURE 1

Options for direct ocean disposal of CO_2

Disposal scenarios that are the focus of current research include droplet plume and dense plume dissolution, dry ice and towed pipe dispersion, and isolation as a dense lake of CO_2 on the sea floor. Towed pipe and droplet plume scenarios may offer the best approach in the near future.

From Hanisch (1998)

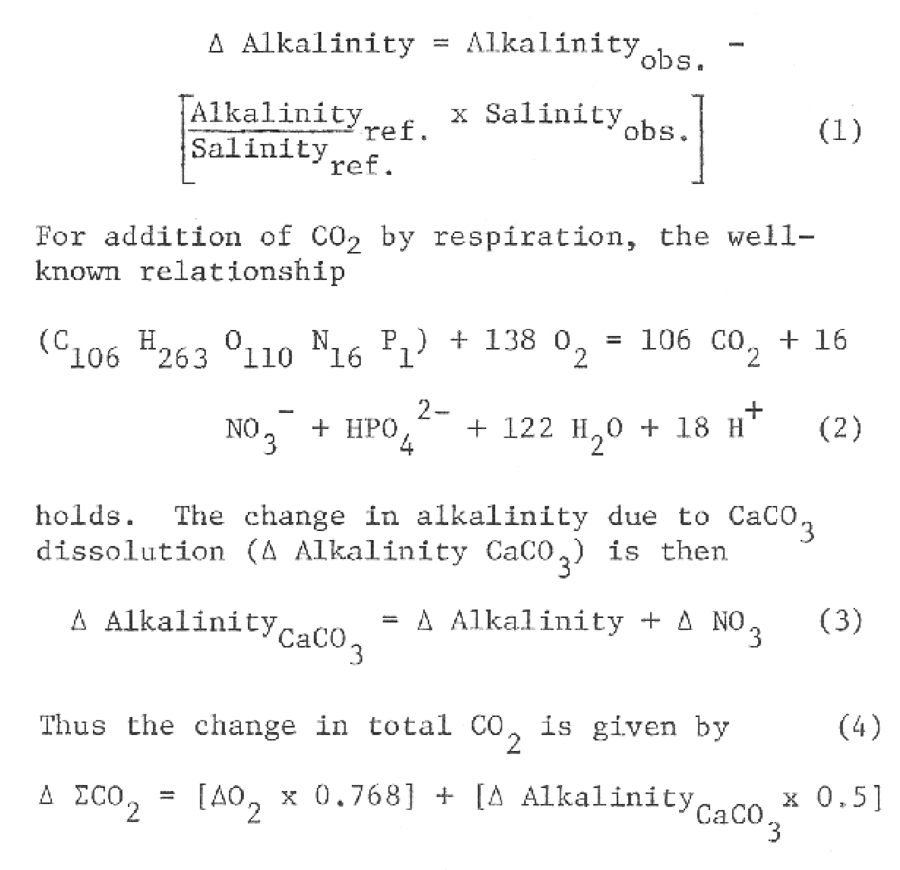
Typical 1990s cartoon sketch of ocean CO_2 disposal scenarios.

The field has changed enormously over the last 4 years. Significant field, laboratory, and numerical experiments have been carried out, programs created, and major international conferences exist on CO_2 disposal technologies.

The policy area is cloudy.

The FACE system in Wisconsin as an example of a CO_2 enrichment expt. of very large scale. For oceanic studies the different fluid dynamics, phase behavior, and biogeochemical systems studied might dictate arrays of 1-10% of this size, but would require at least as many replicates.

Direct Observation of the Oceanic CO_2 Increase – *Brewer (1978)*



$$\Delta \text{ Alkalinity} = \text{Alkalinity}_{\text{obs.}} - \left[\frac{\text{Alkalinity}_{\text{ref.}}}{\text{Salinity}_{\text{ref.}}} \times \text{Salinity}_{\text{obs.}}\right] \quad (1)$$

For addition of CO_2 by respiration, the well-known relationship

$$(C_{106}\ H_{263}\ O_{110}\ N_{16}\ P_1) + 138\ O_2 = 106\ CO_2 + 16\ NO_3^- + HPO_4^{2-} + 122\ H_2O + 18\ H^+ \quad (2)$$

holds. The change in alkalinity due to $CaCO_3$ dissolution (Δ Alkalinity $CaCO_3$) is then

$$\Delta \text{ Alkalinity}_{CaCO_3} = \Delta \text{ Alkalinity} + \Delta\ NO_3 \quad (3)$$

Thus the change in total CO_2 is given by (4)

$$\Delta\ \Sigma CO_2 = [\Delta O_2 \times 0.768] + [\Delta \text{ Alkalinity}_{CaCO_3} \times 0.5]$$

The method was first applied to a south Atlantic Geosecs leg. Over 25 years later the signal is now so enormous that it is unmistakable. We have entered the oceanic anthropocene era.

This paper was the first explicit recovery of the ocean fossil fuel signal. It was criticized since the signal was so small compared to background that the errors might be large. Yet this remains the foundation of all modern signal recovery techniques.

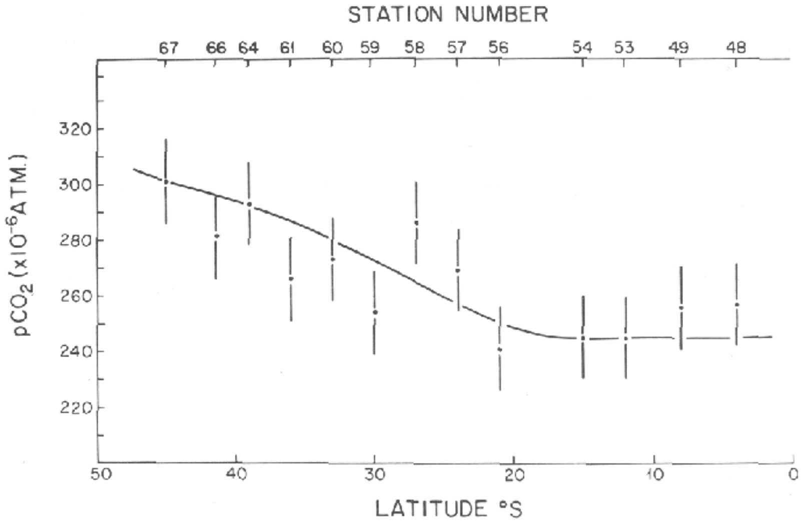
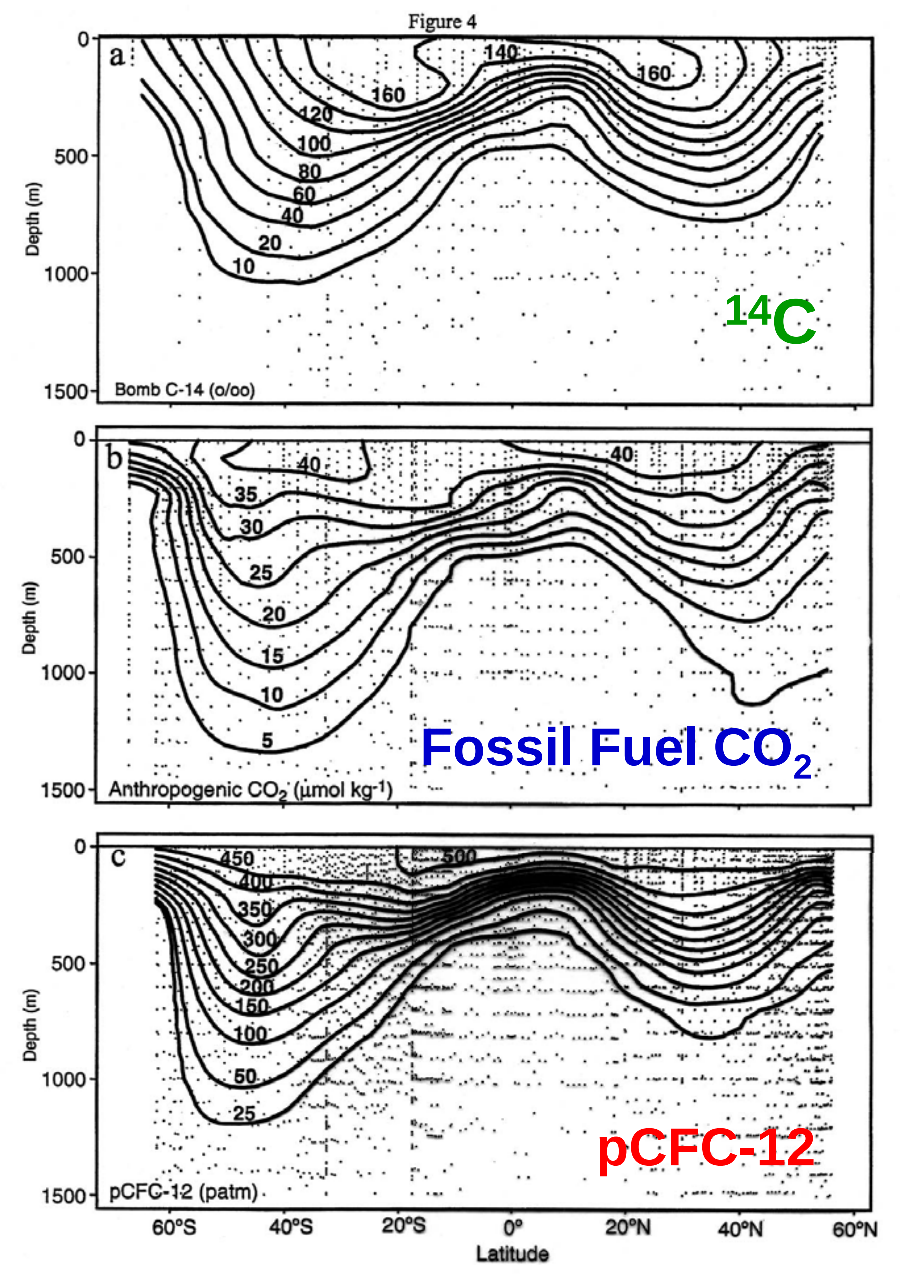


Fig. 2. The calculated initial pCO_2 of samples taken at the core of the salinity minimum of the Antarctic Intermediate Water in 1972.

Ocean CO_2 “Disposal” Today



From Sabine et al. 2002:

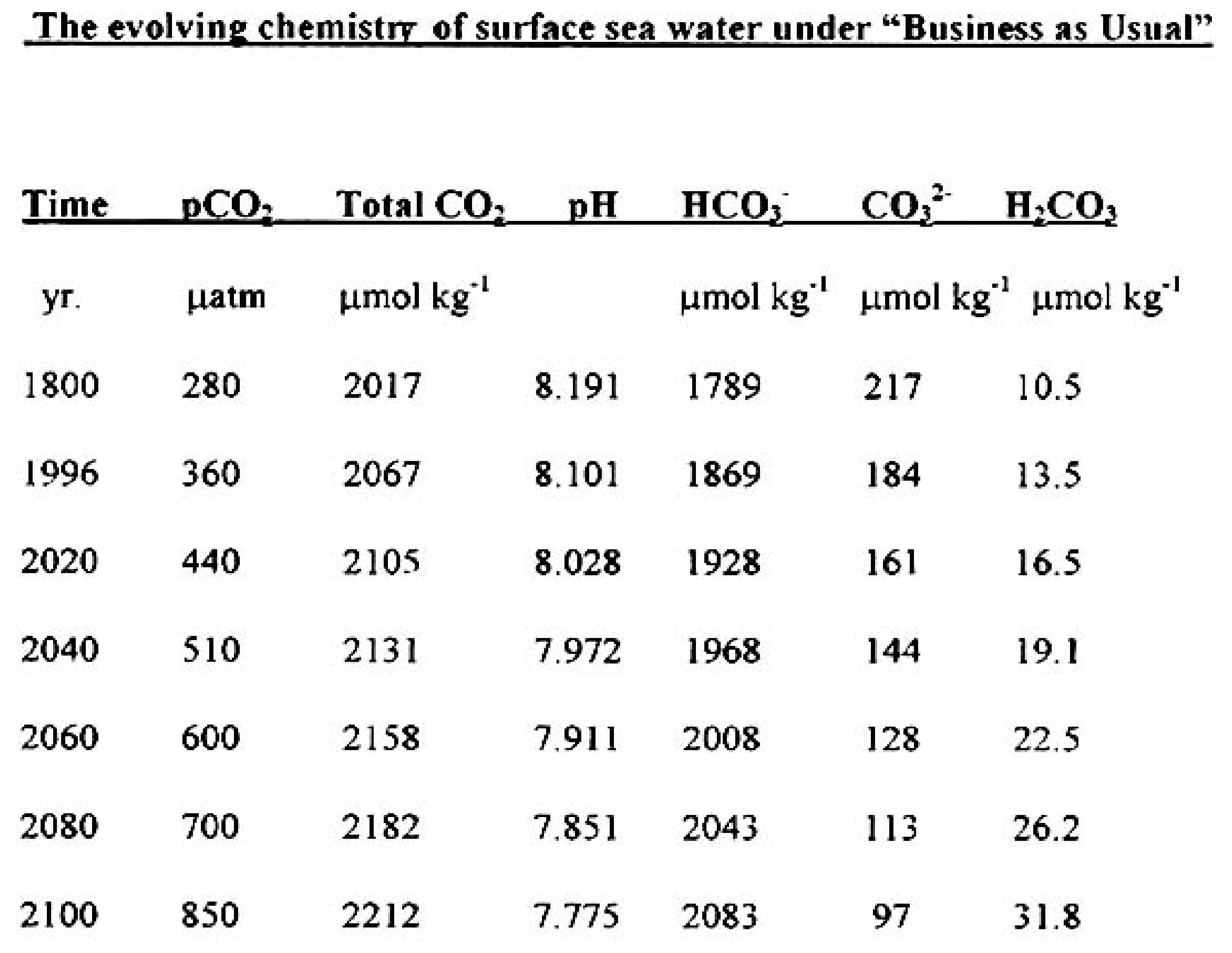
JGOFS/WOCE survey data. Pacific meridional section.

Fossil fuel signal has penetrated to >1000m. Surface values reach 50µmol/kg (2.2 mg/kg). The inventory is 44.5±5 Pg C in 1994.

We have disposed of ~ 163 billion tons of CO_2 in Pacific Ocean waters.

The ocean now has taken up ~500 GT of fossil fuel CO_2.

Global surface ocean CO_2 disposal is now about 20-25 million tons per day - about 1 million tons per hour.



The evolving chemistry of surface sea water under "Business as Usual"

Time	pCO_2	Total CO_2	pH	HCO_3^-	CO_3^{2-}	H_2CO_3
yr.	µatm	µmol kg^{-1}		µmol kg^{-1}	µmol kg^{-1}	µmol kg^{-1}
1800	280	2017	8.191	1789	217	10.5
1996	360	2067	8.101	1869	184	13.5
2020	440	2105	8.028	1928	161	16.5
2040	510	2131	7.972	1968	144	19.1
2060	600	2158	7.911	2008	128	22.5
2080	700	2182	7.851	2043	113	26.2
2100	850	2212	7.775	2083	97	31.8

From Brewer, 1997

"Why are you mentioning this – climate is the problem, not pH "

Under IPCC "Business as Usual"the pH of surface sea water drops by 0.4 pH units by 2100. $CO_3^=$ in surface water drops by 55% from pre-industrial values. It will be hard to meet even these goals.

Fossil fuel CO_2 is now a major ion of sea water.

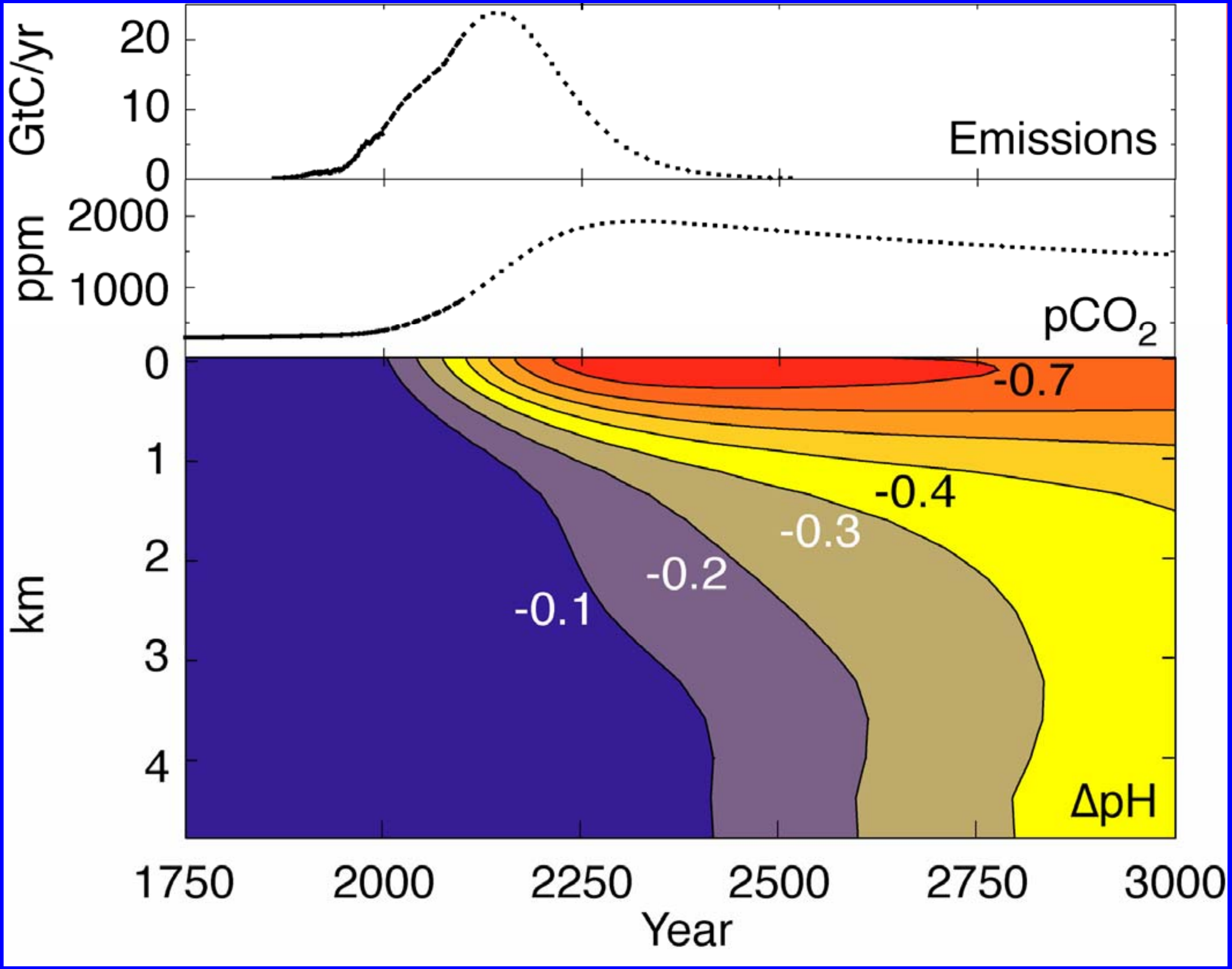
An early CO_2 sequestration experiment (Brewer et al. 1999)

There are few beakers on the normal ocean floor! – yet we continue to use contained CO_2 pools for experimental convenience and control.

If we are to extend this research to simulate real situations then we must create the skills to deal with freely released CO_2 in much the same way as is done on land.

The complex self-generating fluid dynamics of this experimental release have not occurred in repeats of this study. The quasi-chaotic nature of hydrate nucleation and growth may be forced by very small changes in initial conditions.

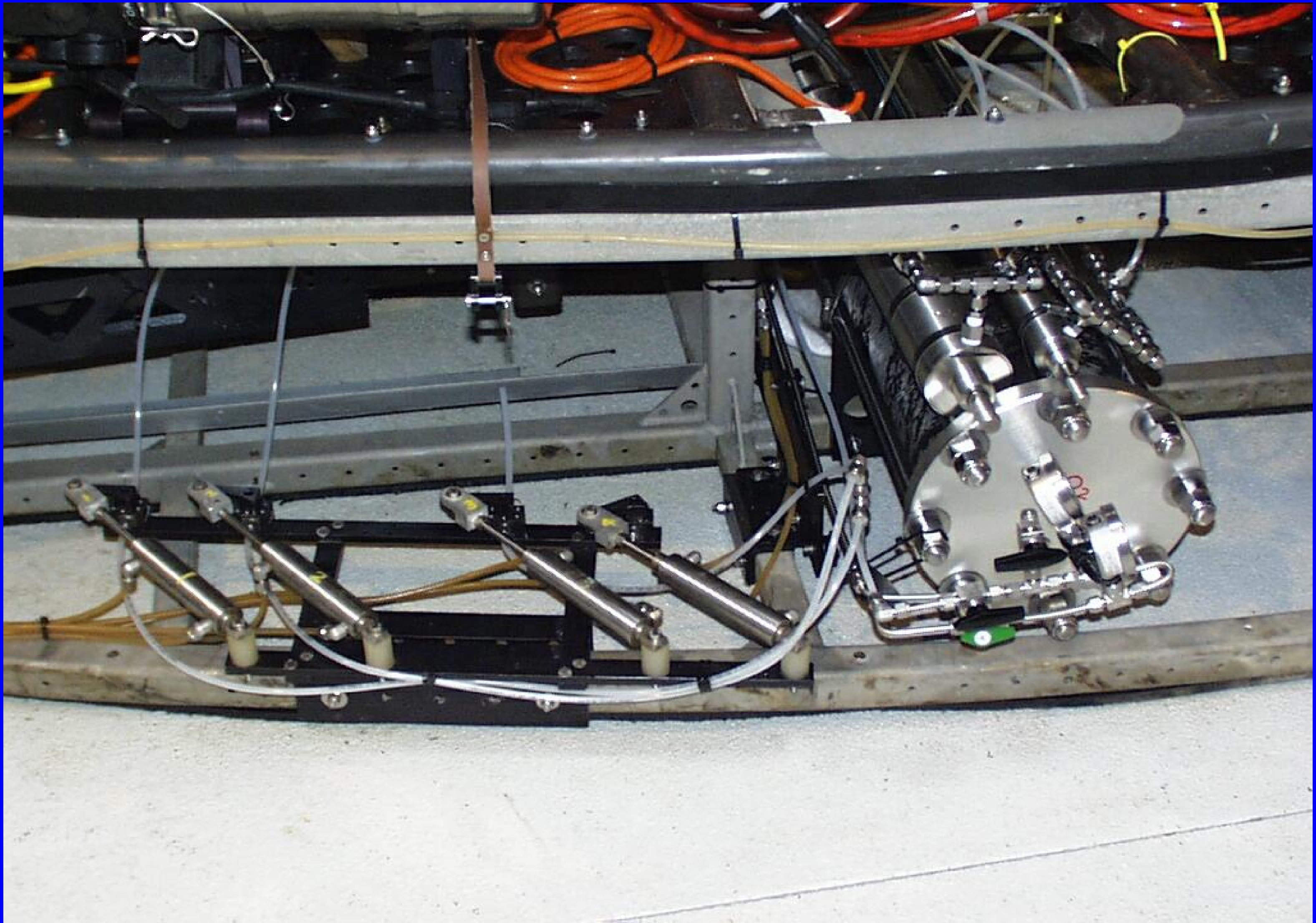
A simulation of changes in ocean pH assuming IS92A and then continued usage of known fossil fuel reserves. Large surface pH changes occur.



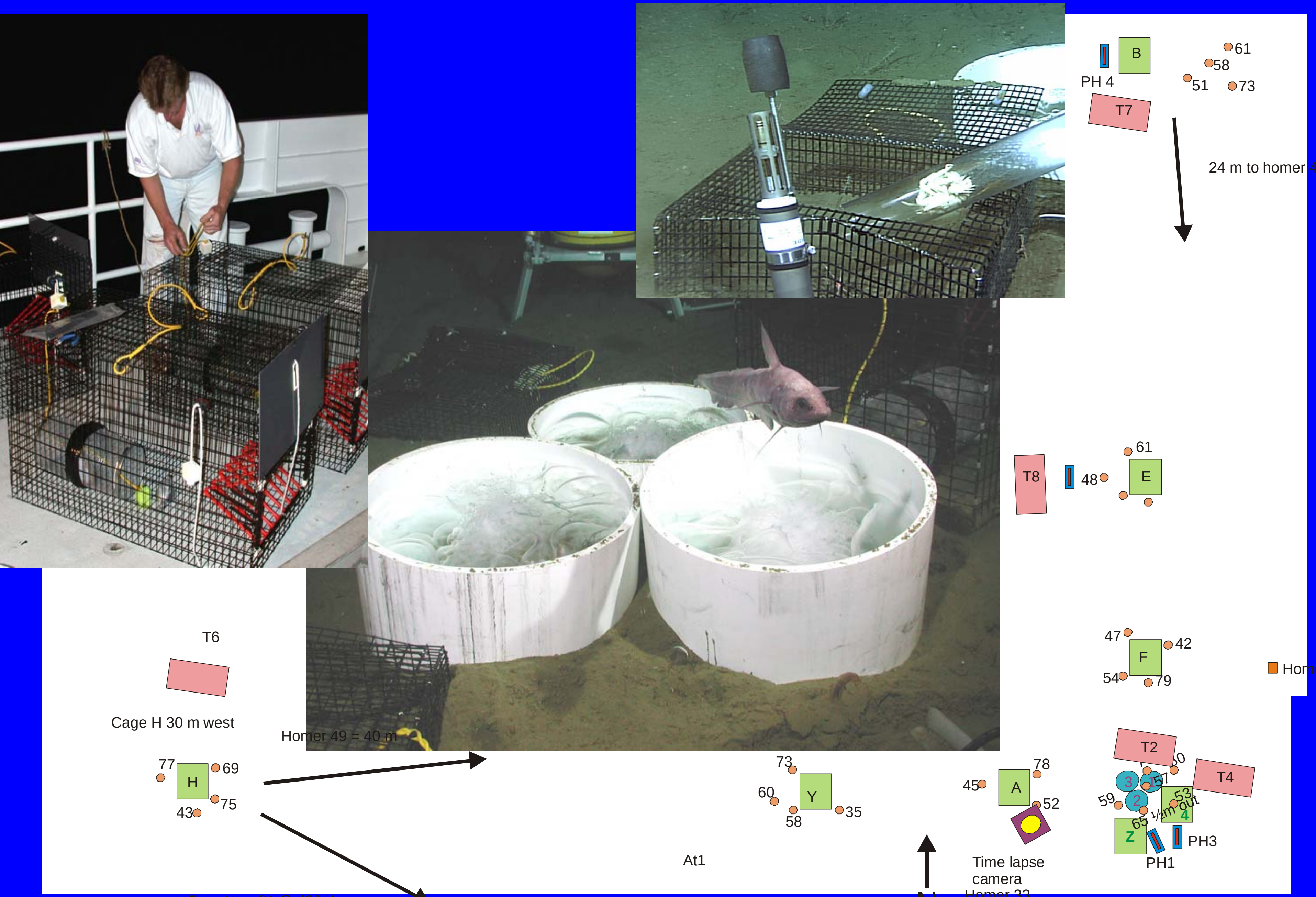
From: Caldeira and Wickett (2003)

Technique Development:

MBARI 56 liter volume (surface) carbon fiber wound accumulator installed on ROV toolsled showing delivery pumps (top), and release valves (left).

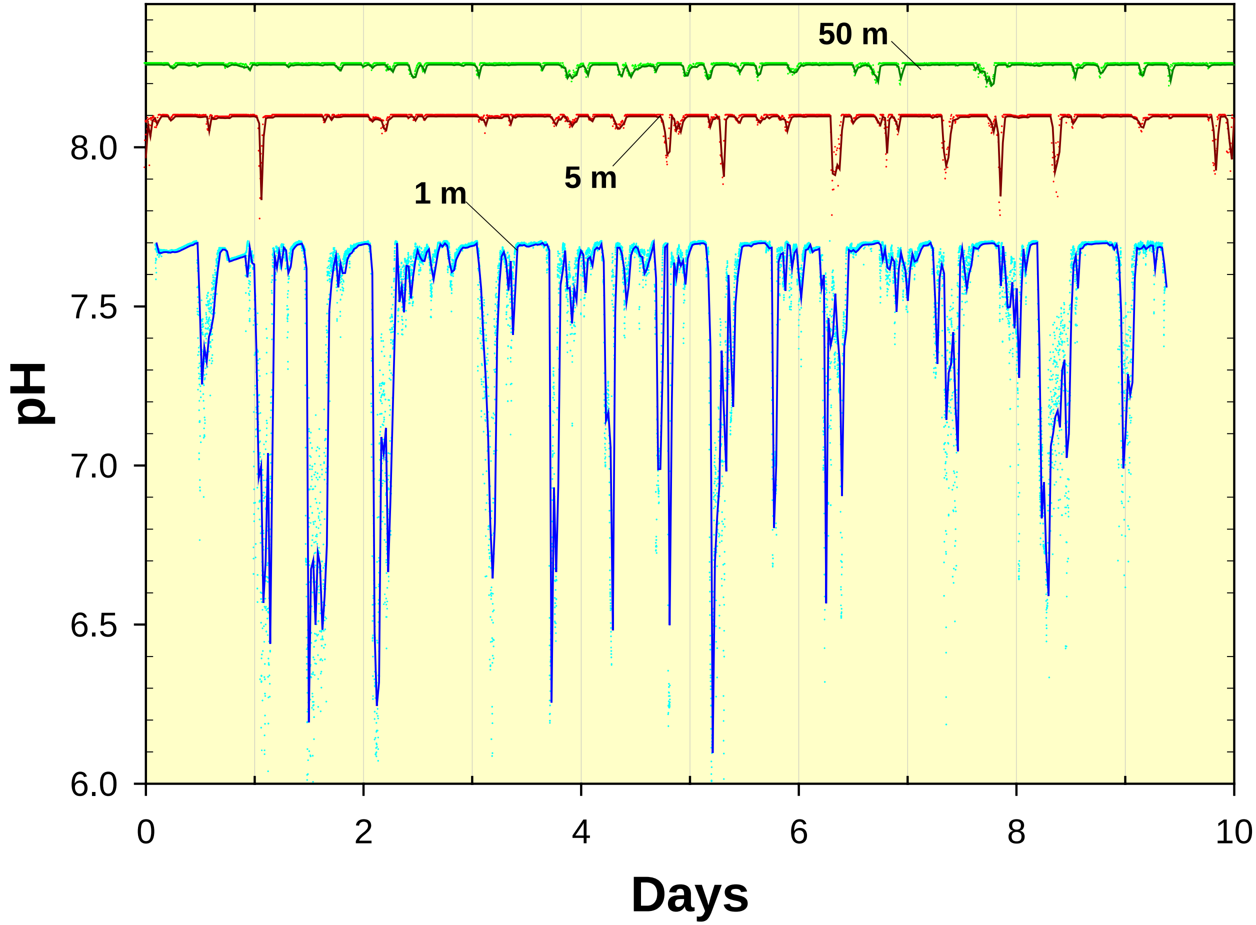


CO2 release exp. II – Oct. – Dec. 2001



Data fragment over 10 days from recording pH sensors at 1, 5, and 50m distance from the central CO_2 corral site. The instrument drift has been removed, and the baseline data normalized to true ocean background values.

From Barry et al. (2003)



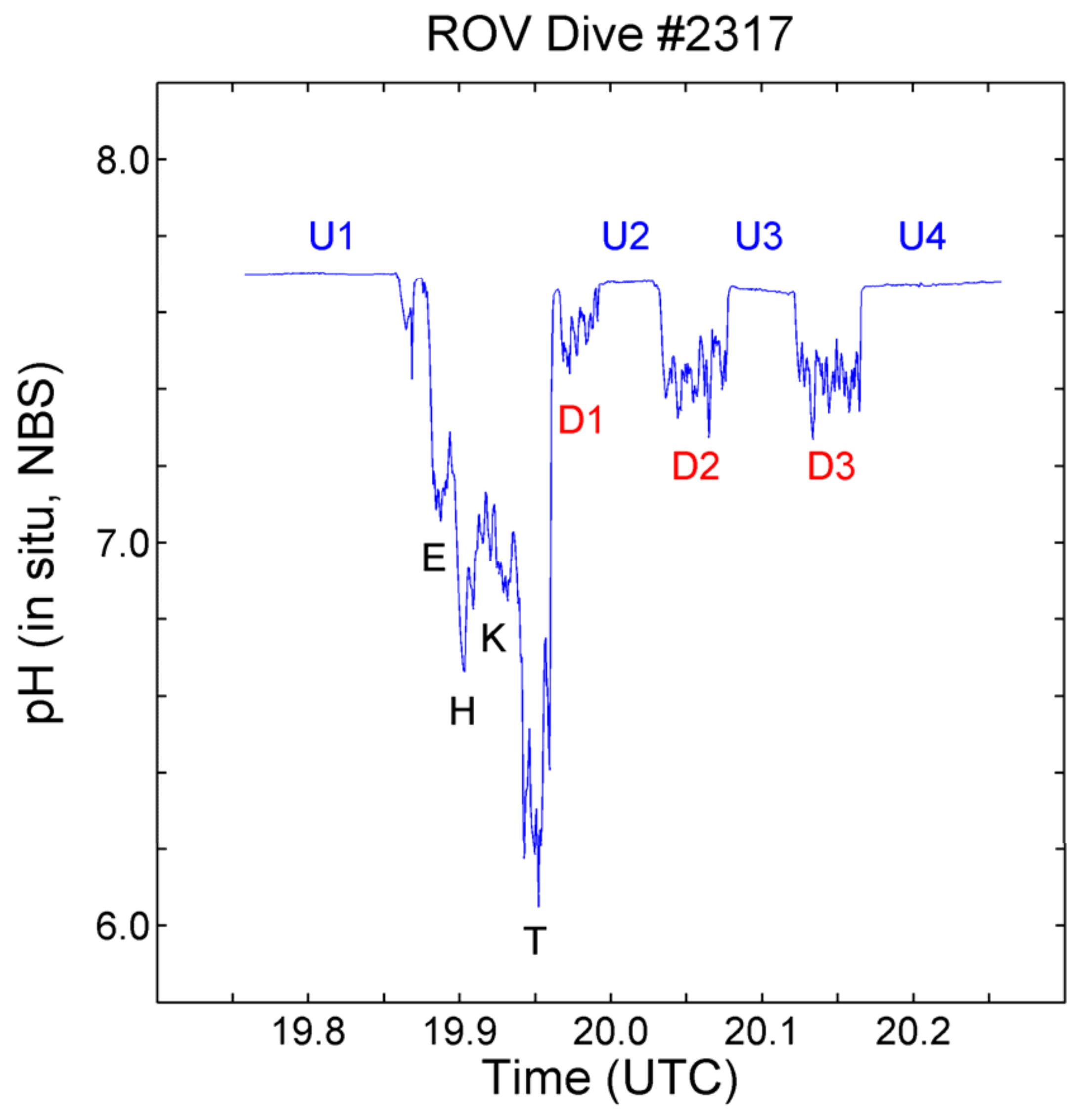
View of the OACE1 experiment. The frame is 120cm high, the base of the box is 103cm above the sea floor. The box is 47 cm square, with walls 23 cm high. The pH-CTD frame is seen immediately behind the frame; a second set of sensors is 2 m away. Depth = 650m. *From Brewer et al. In Press.*

The experiment was designed to test the signature of the dense low pH plume from the CO_2 pool.

- ***A sinking plume?***
- ***CO_2-H_2O reaction rates?***
- ***Sensor stability?***
- ***pH sensitive dye?***
- ***Effect of ocean currents on the interface?***

The erratic nature of the flow field, and eddies induced by the structure make plume sensing difficult with these small scale systems – by moving the electrode around the source we can measure the signal strength, noise levels, boundary layer influence etc. Here the inverted pH electrode is held close to the CO_2-water interface.

Results from pH sensing of the plume from the OACE 1 experiment: Direct electrode placement.



pH values were calibrated and reported on the NBS scale. The probe was placed upstream, inside the box, and downstream.

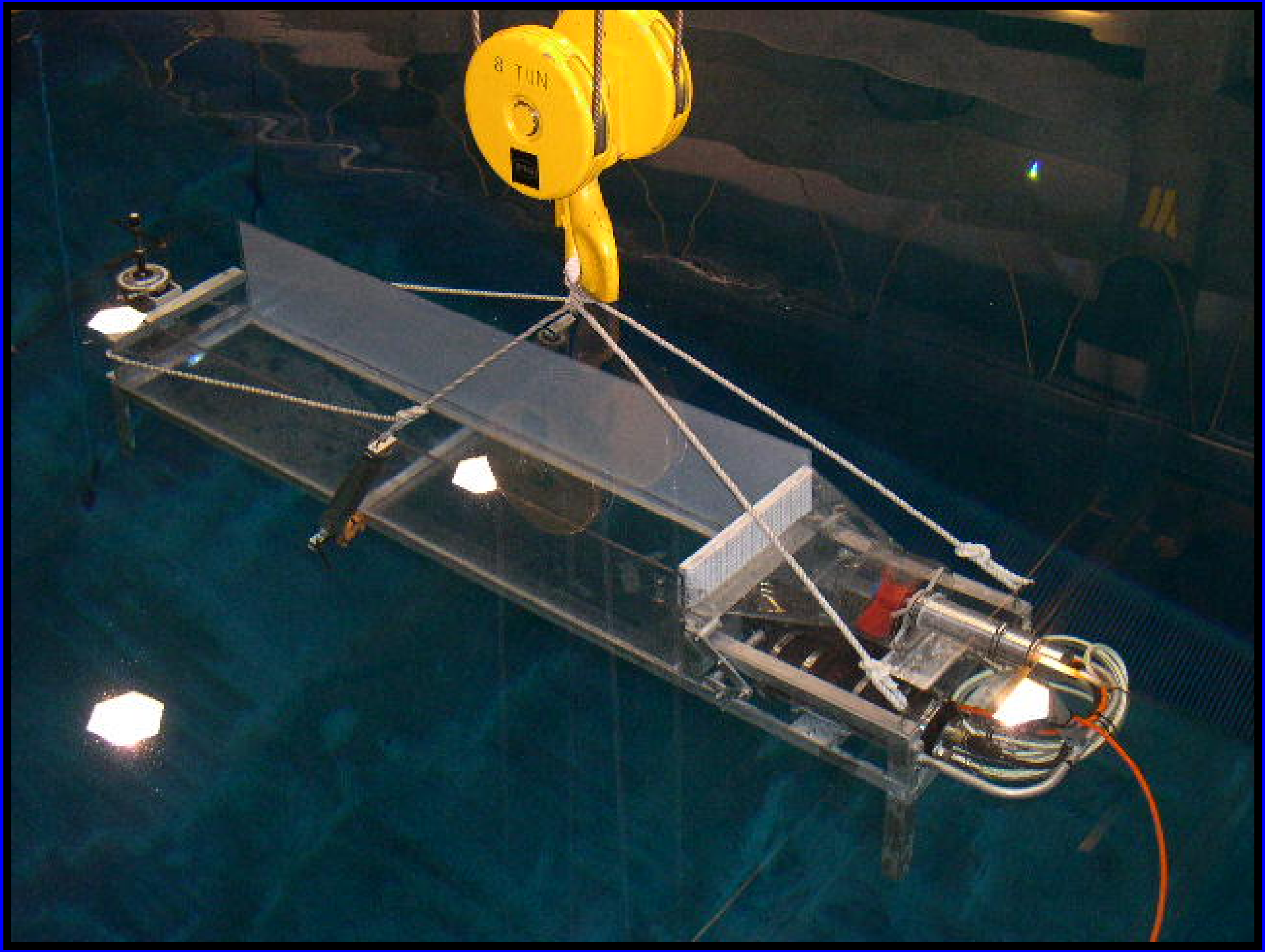
- ***Upstream (U 1-4) values were 7.701 ± 0.001 (U1) to 7.670 ± 0. 002 (U4). The field is observed with high precision.***

- ***Downstream (D 1-3) values showed a turbulent plume of pH 7.547 ± 0.069 (D1) to 7.426 ±0.056 (D3).***

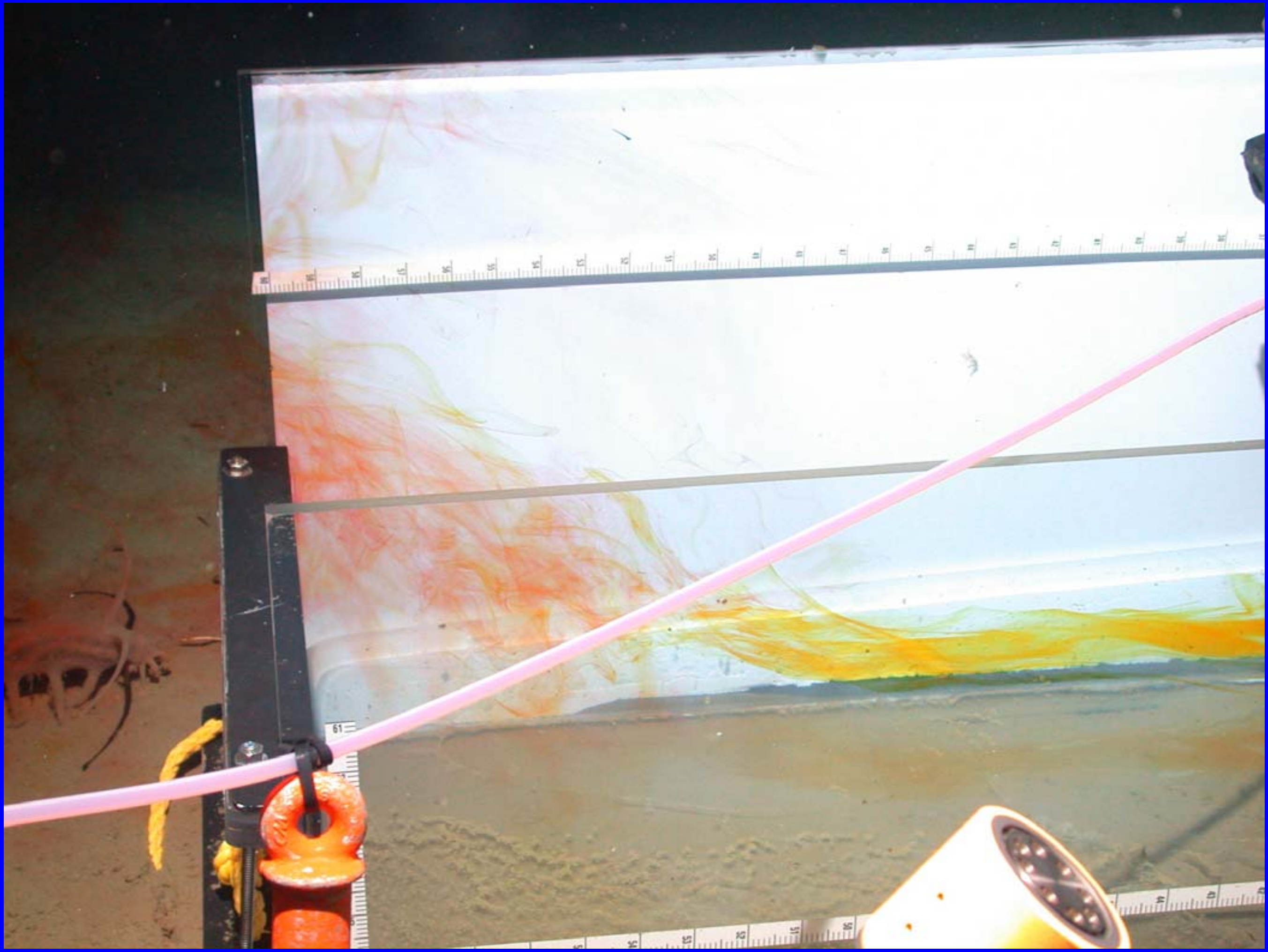
- ***Values inside the box showed a thin boundary layer with low values of pH ≅ 6.0***

Creation of a controlled plume of high CO2 – low pH water

The OACE 4km flume experiment – a small trough equipped with a wave generator, and a controllable thruster was placed on the sea floor, and partially filled with CO_2. By activating the thruster we could induce gravity waves on the liquid surface and force a directed plume for sensor (pH,CTD) detection downstream.

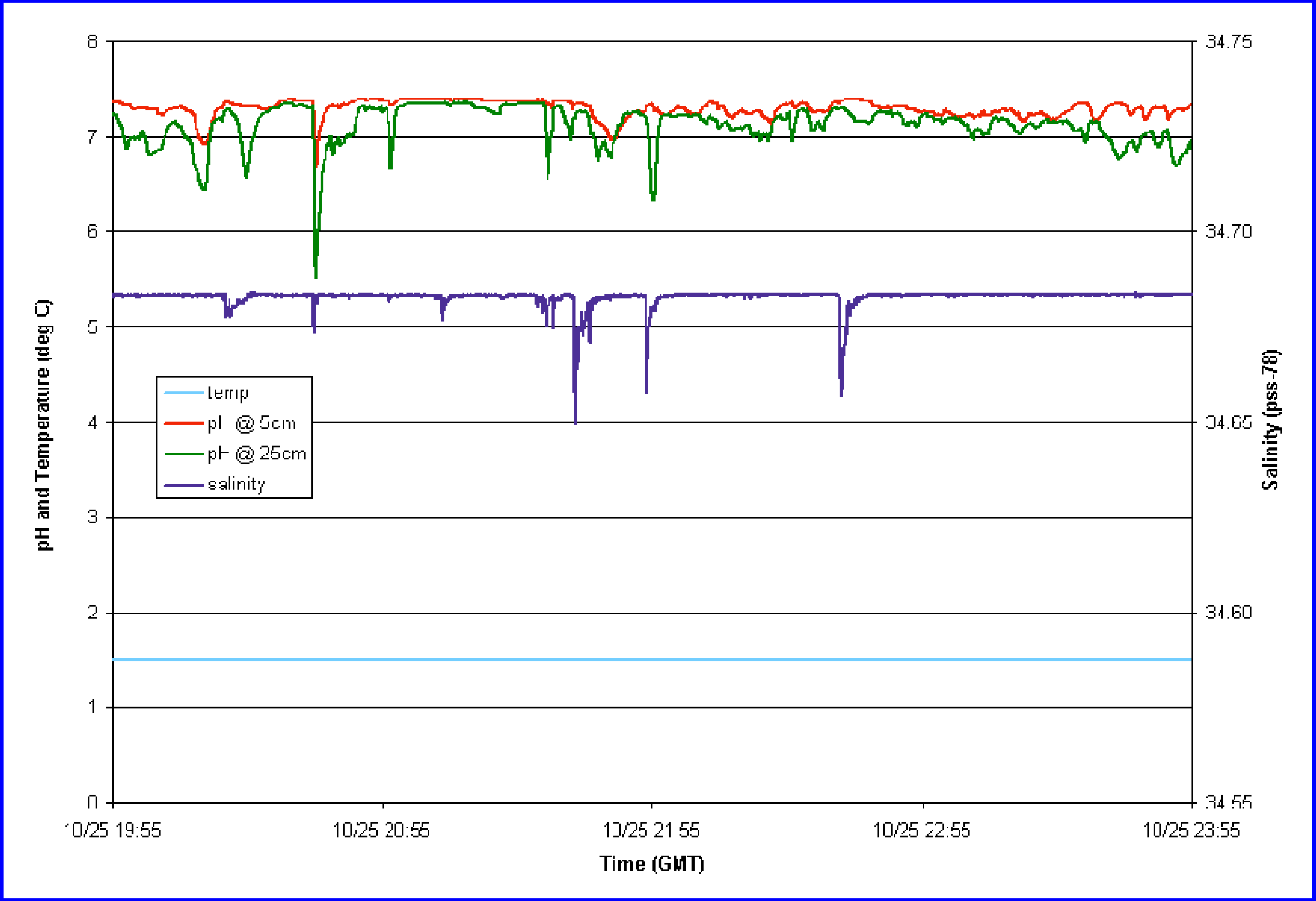


OACE 2 at 3940m – a phenol red dye shows the dense low pH boundary layer mixing upwards at the end of an experimental trough. The indicator changes From yellow (pH<5.2) to red (pH>6.8). Such techniques allow us to visualize the flow and place sensors in the plume.



Data fragment from the plume sensing experiment. The low pH signal is recorded by the electrode, but the CTD records a conductivity decrease! This can only be due to the dilution effect of unreacted CO_2 passing by the electrode.

The effect of increased HCO_3^- is to increase conductivity*(Brewer & Bradshaw, 1975)* ***and we thus have a complex CO_2 + HCO_3^- plume not at equilibrium.***



Analyzing the plume signal by combining pH and conductivity

The total CO_2 content of the water flowing past the conductivity sensors may be approximated as:

$$\Delta TCO_2 = f(\Delta \text{conductivity}) + f\,(\Delta \text{pH})$$

Since the effect of free CO_2 is to reduce the conductivity, and the effect of adding HCO_3^- is to increase it, then the true change in CO_2 can be given as:

$$\Delta TCO_2 = f(\Delta \text{conductivity observed} + \Delta \text{conductivity } HCO_3^-) + HCO_3$$

For the free CO_2 molecule:

The conductance effect is due to the volume fraction (φ) of the obstructing electrolyte (Einstein, 1911) ***and 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.***

For the HCO3- ion:

Substituting the value for $\Lambda_{NaHCO3-}$ from Connors and Weyl (1968) we then find

$$\Delta S\%_0 = 0.060 \text{ per mol. } 10^{-3}/\text{kg } CO_2$$

Solving the puzzle

The change in TCO_2 of the water flowing past the conductivity and pH sensors is:

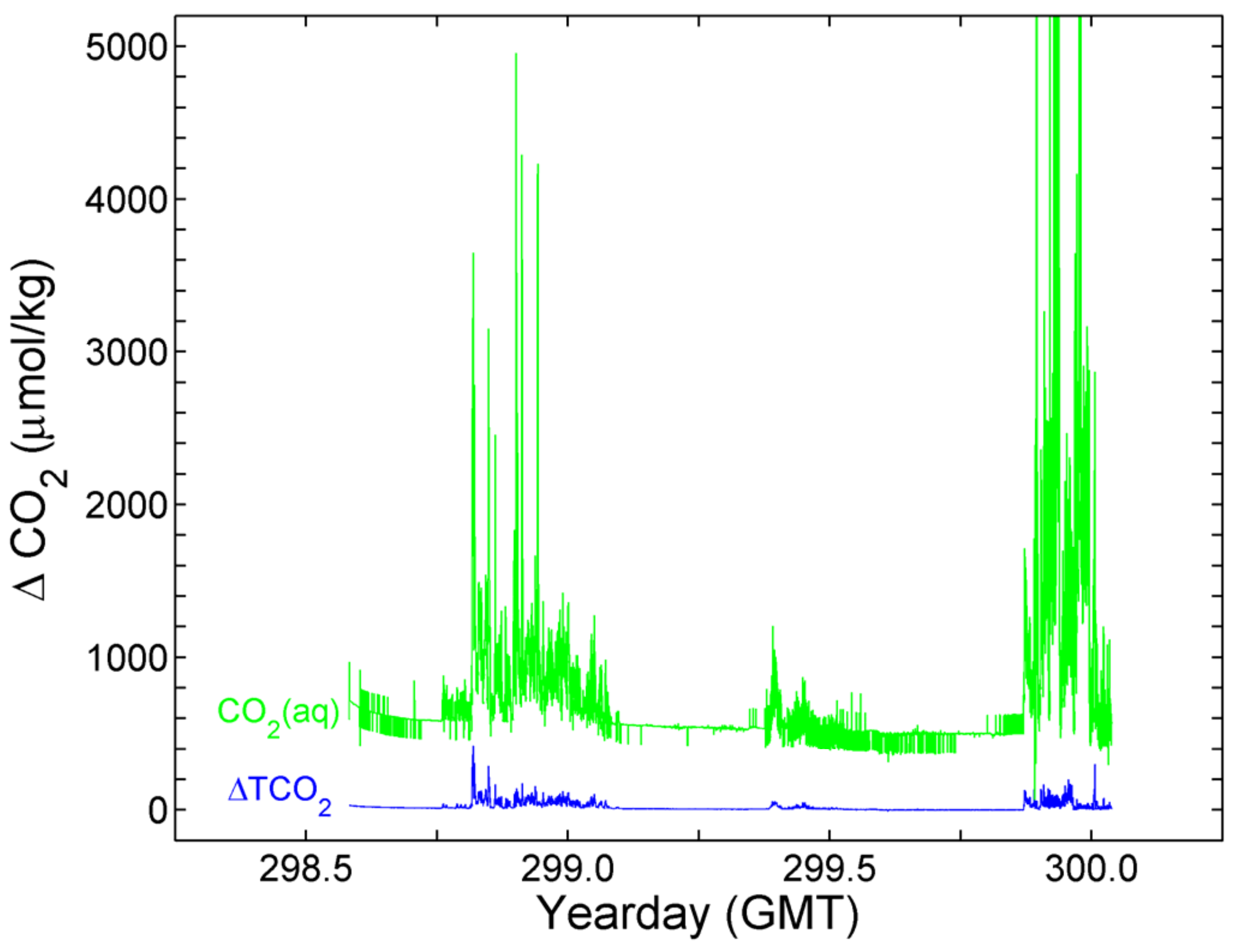
$$\Delta TCO_2 = \Delta HCO_3^- + \Delta CO_2^*$$

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

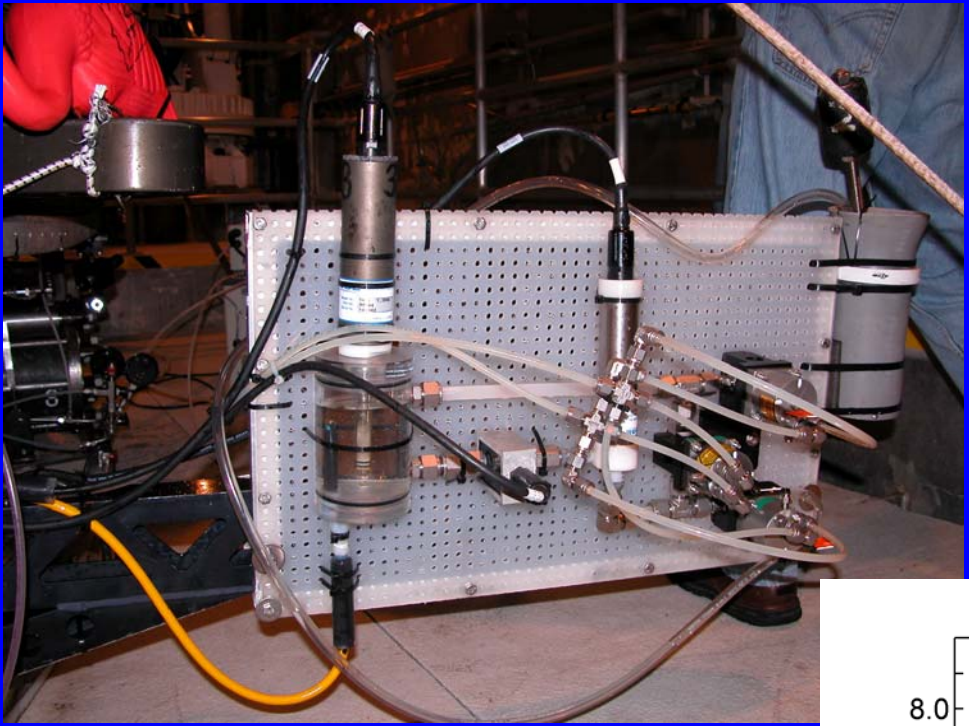
$$\Delta HCO_3^- = \frac{\Delta pH_{measured}}{\left(\dfrac{\delta pH}{\delta HCO_3^-}\right)_{calculated}}$$

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

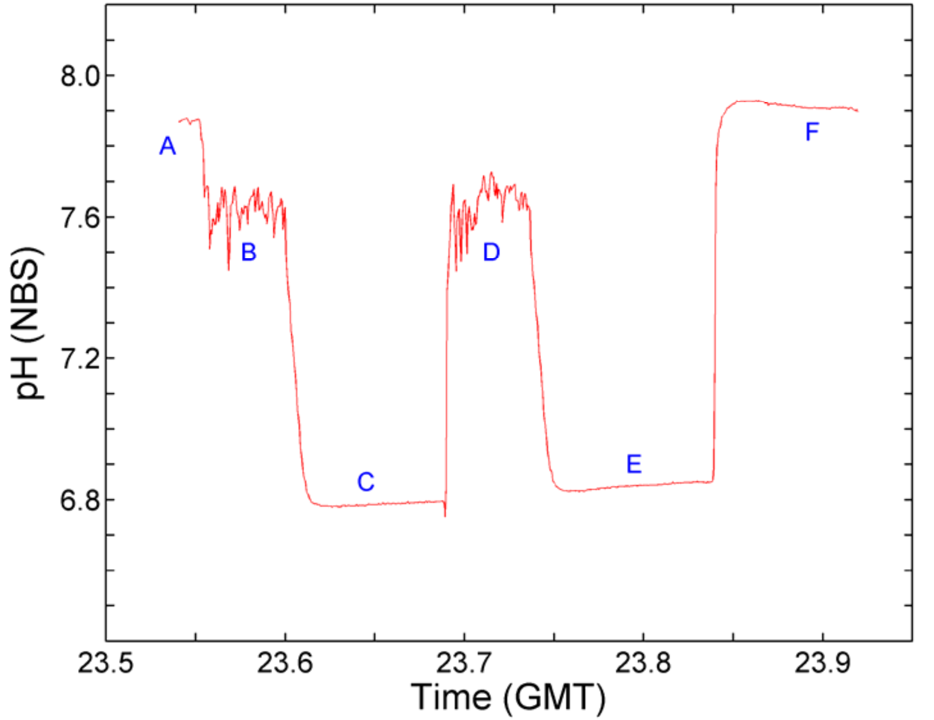
$$\Delta Cond_{measured} = \left(\frac{\delta Cond}{\delta HCO_3^-}\right) \times \Delta HCO_3^- + \left(\frac{\delta Cond}{\delta CO_2^*}\right) \times \Delta CO_2^*$$



The record of CO_2aq deduced from the conductivity record, and the change in TCO_2 as HCO_3^-. Both sensors are about 30cm distant from the CO_2 source. The CO_2 aq signal clearly dominates, and the ratio will shift downstream as the hydration-ionization process occurs. *From Brewer et al. 2004.*



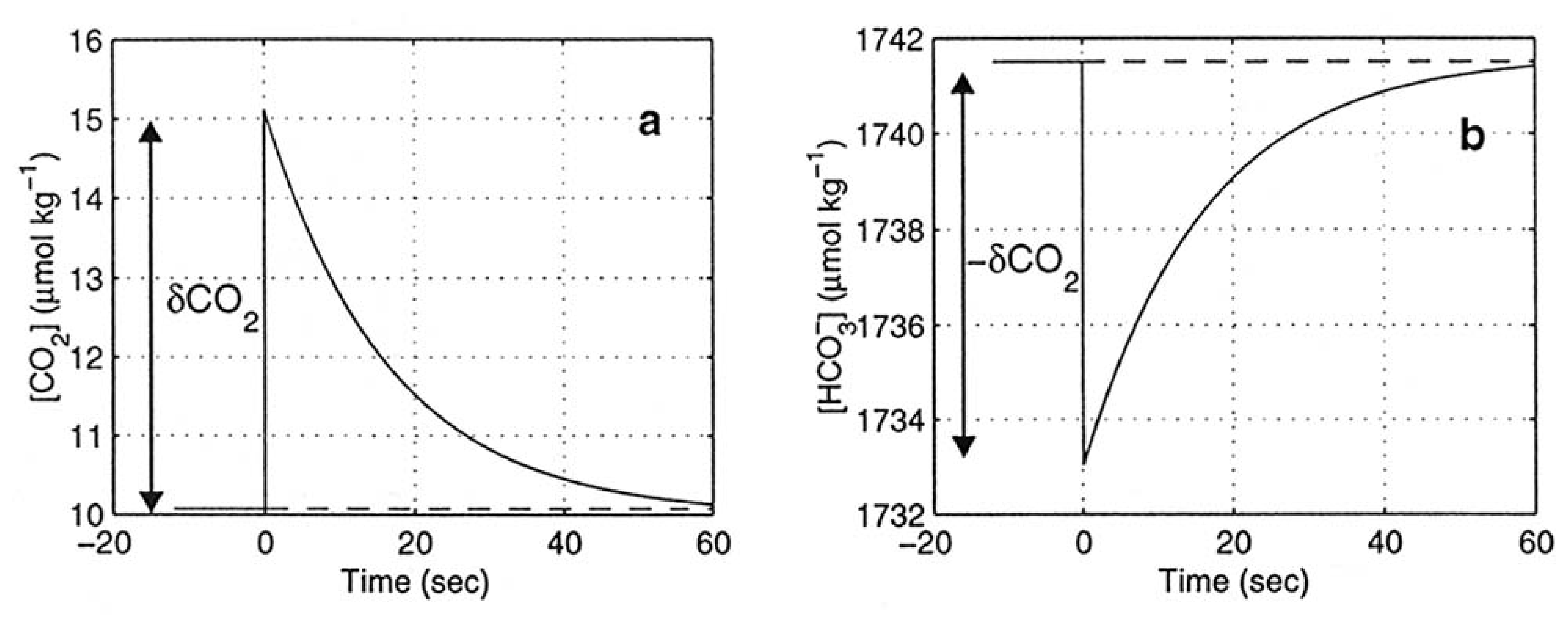
A simple kinetic test. Sea water is drawn into the pH cell, the valves are closed and the time to reach pH equilibrium in the flow loop is observed.



Results from two sample runs in the plume from a flume at 3960m depth. The noisy signal in the plume quickly drops to a lower pH. The plume pH is not at equilbrium – but at this T at I atm it would take ~20 minutes for equilibrium to be achieved! Here it Is achieved in ~30 seconds.

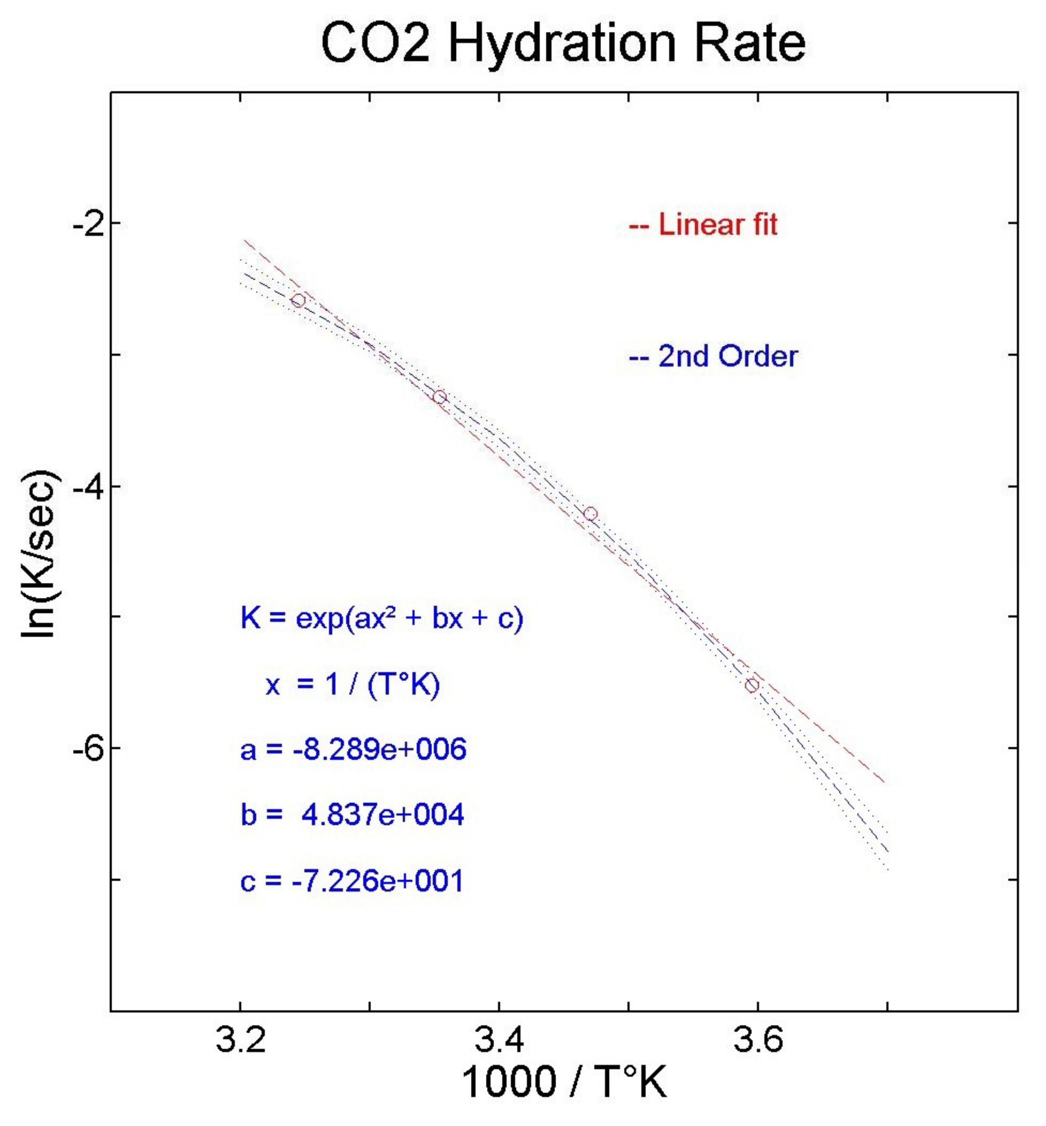
From Zeebe et al. (1998)

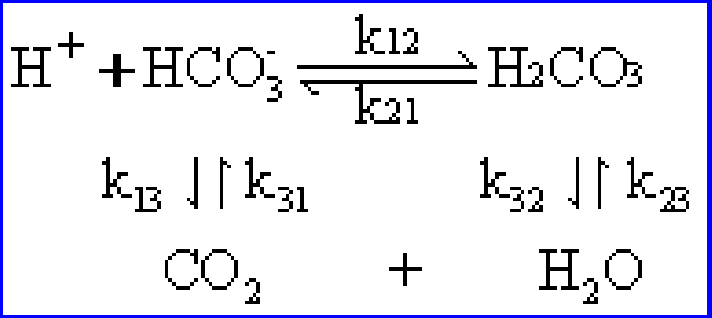
Time required (25°C, 1 atm.) for equilibrium in the ocean CO_2 system. At 1-2°C we may expect about a factor of 4-5 times longer, or several minutes. At velocities of 10cm/sec this implies dis-equilibrium for a zone about 3 meters around our corrals where pH underestimates the concentration of CO_2.



For CO_2 disposal we must use CO_2 itself. To simulate the emerging low pH ocean we may use acid addition to lower pH; there are kinetic challenges.

The CO_2 hydration rate constant *(Johnson,1982)*





$$\begin{tikzcd} H^+ + HCO_3^- \arrow[rr, shift left, "k_{12}"] \arrow[d, shift right, "k_{13}"'] & & H_2CO_3 \arrow[ll, shift left, "k_{21}"] \arrow[d, shift right, "k_{32}"'] \\ CO_2 \arrow[u, shift right, "k_{31}"'] & + & H_2O \arrow[u, shift right, "k_{23}"'] \end{tikzcd}$$

These data are for 1 atmos. They imply a time to equilib. of ~15 minutes at 1.6°c, and this reaction time is far beyond our observation site. However the dissolution of CO_2 produces a strong $-\Delta V$, and thus the effec of pressure is to shift the equm. to the hydrated state – but the <u>rates</u> at pressure are unknown.

Analysis in terms of transition state theory

Human Carbonic Anhydrase – an ultra-fast zinc metalloenzyme for HCO3 ↔ CO2

The essential function of an enzyme is to stabilize the transition state. The form of the CO_2-H_2O transition state has not been identified.

Mechanism? – Still debated
A Zn-bound OH^- ion is assumed to attack a CO_2 molecule giving HCO_3^-. The Zn atom is buried in a deep cleft in the enzyme, allowing it to strip the OH^- ion of its solvation sphere, at the same time keeping it stable relative to protonation, since there is little room in the cleft for effective solvation of the $ZnOH^+$ moiety.

Jonsson et al. (1978)

Ab Initio Molecular Orbital Calculations on the Water-Carbon Dioxide System: The Reaction $OH^- + CO_2 \rightarrow HCO_3^-$. From Jonsson et al. 1978.

An unusually long C-OH distance of 1.43 Å emerged.

There is no potential energy barrier for for the formation of HCO_3^- from CO_2 and OH^- in the gas phase, so the slow rates in solution must be due to solvation effects.

The transition state identified in the gas phase Is also valid for the $CO_2 + H_2O$ reaction path.

The critical feature for ocean chemistry is the effect of T and P on the hydration sphere of the dangling proton

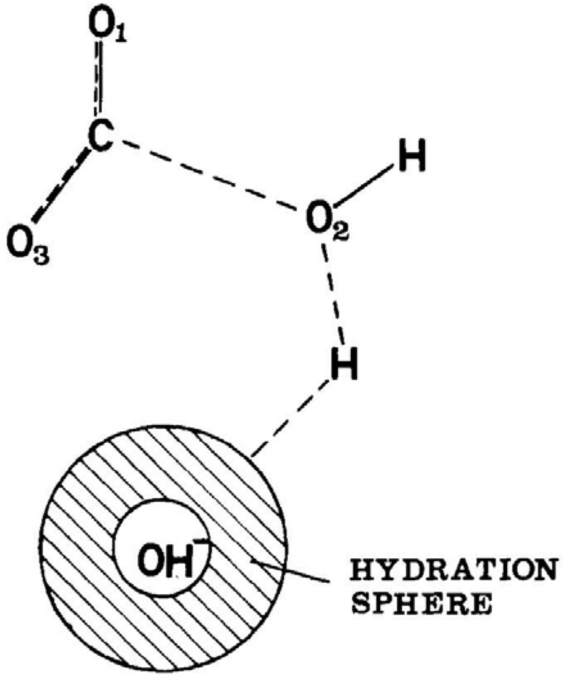


Figure 4. A possible transition state for the $OH^- + CO_2 \rightarrow HCO_3^-$ reaction in aqueous solution.

The Effect of Pressure on the Chemical Properties of Sea Water

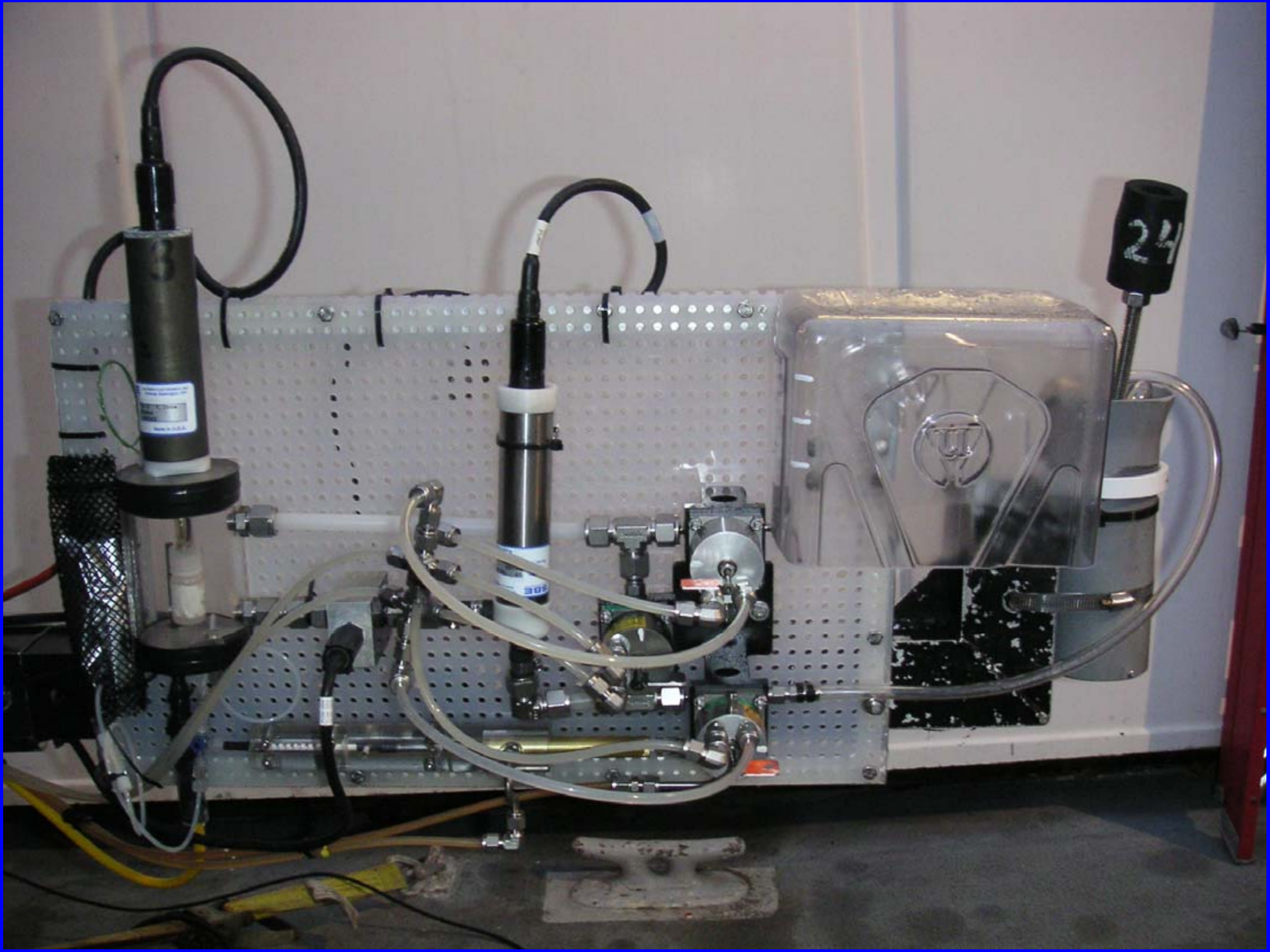
We can readily calculate the effect of pressure on the equilibrium state through knowledge of the equilibrium constants and the partial molal volume change for the reaction:

$$\left(\frac{\partial \ln K}{\partial P}\right)_T = -\frac{\Delta V^o}{RT}$$

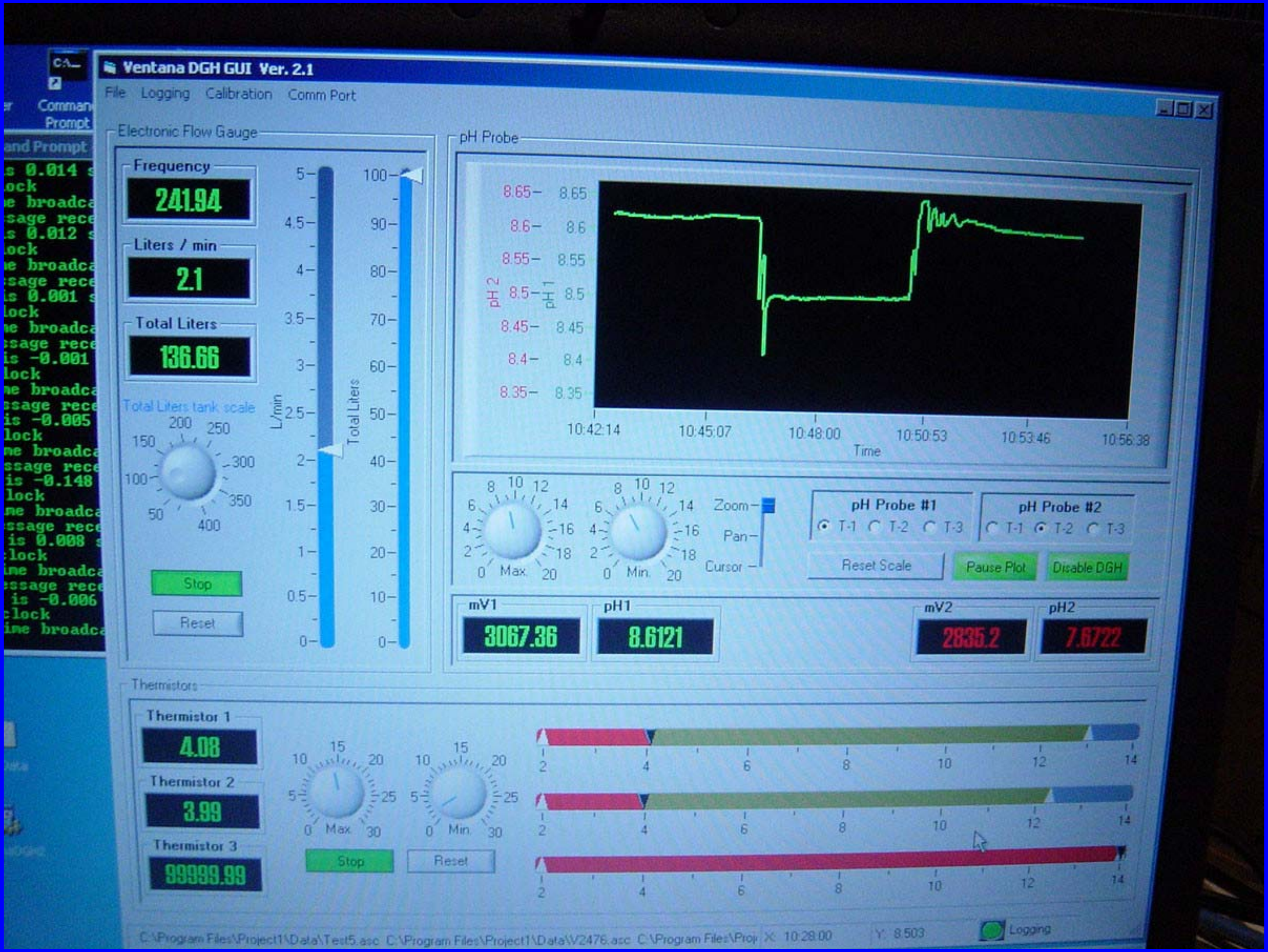
For the reaction of CO_2 with sea water we have a large ΔV of –31 cm^3/mol, and thus we expect pressure to shift the system towards the lower volume state and favor the reaction.

But we cannot predict the effect of pressure on the reaction rate – that must be determined experimentally.

MBARI pH equilibration cell for flow through, and looped circulation, to observe the time for achieving pH equilibrium at depth. A small syringe for acid injection is mounted at the bottom, a container for CO_2 is at right.



The slow hydration kinetics of CO_2 at low temperatures will not limit deep-sea CO_2 enrichment experiments. We have uncovered a very large pressure effect, such that equilibrium is reached in only seconds. Shown here is the effect of adding a small amount of acid to 4°C sea water at 1000m depth. Nakayama et al. In Prep.



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Frequency: 241.94

Liters / min: 2.1

Total Liters: 136.66

pH Probe #1: ● T-1 ○ T-2 ○ T-3

pH Probe #2: ○ T-1 ● T-2 ○ T-3

mV1: 3067.36

pH1: 8.6121

mV2: 2835.2

pH2: 7.6722

Thermistor 1: 4.08

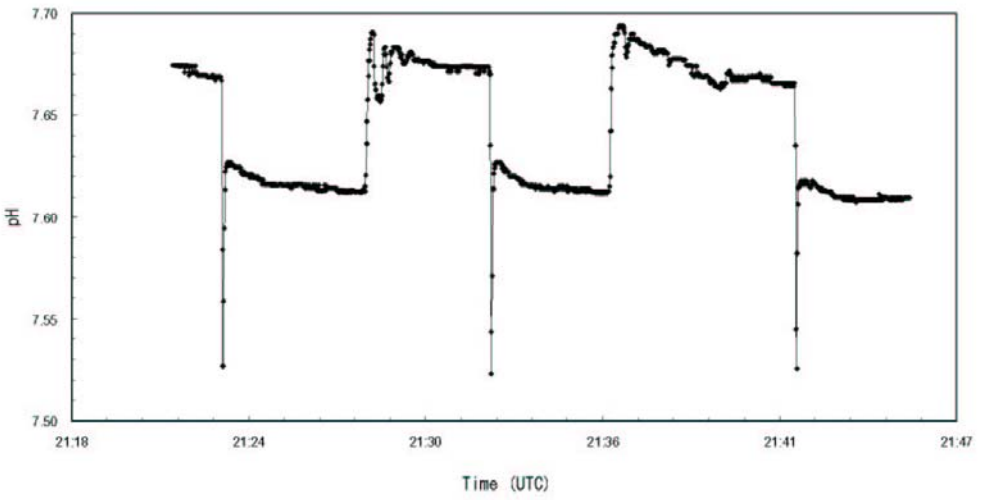
Thermistor 2: 3.99

Thermistor 3: 99999.99

C:\Program Files\Project1\Data\Test5.asc C:\Program Files\Project1\Data\V2476.asc C:\Program Files\Proj X: 10:28:00 Y: 8.503

Results from a 500m depth acid injection experiment to test the feasibility of in situ controlled pH perturbation experiments

Fig. 4

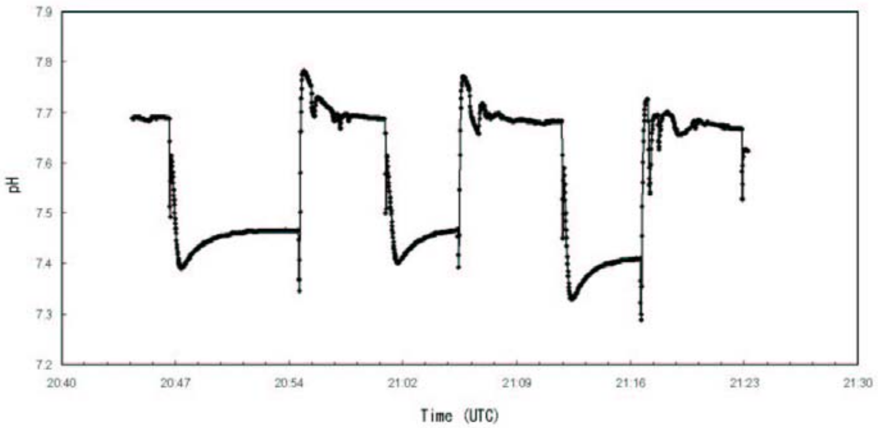


D2476 Injection of HCl at 500m

The data are consistent with formation of an intense cloud of CO_2 at the injection tip, followed by rapid mixing and hydration of the excess CO_2 to form HCO_3^-. This reaction has a volume decrease, and is accelerated by pressure.

Results from an injection of HCO_3^- rich water in contact with a CO_2 pool

Fig. 5



D2476 Injection of CO2 enriched seawater at 500m

The shape of the curve differs from acid injection and is consistent with removal of excess HCO_3^- . This requires a volume increase, and the reaction at depth is slower than for acid addition – but still far faster than at 1 atm.

pH versus time curves for an experiment at 500m depth (6°C) for both acid addition (upper left) and HCO_3^- rich water addition (lower right). The initial rapid change is not fit, only the slower exponential decay at the end.

Note the reversed shape, and slower response of the HCO_3^- curve.

Fig.A

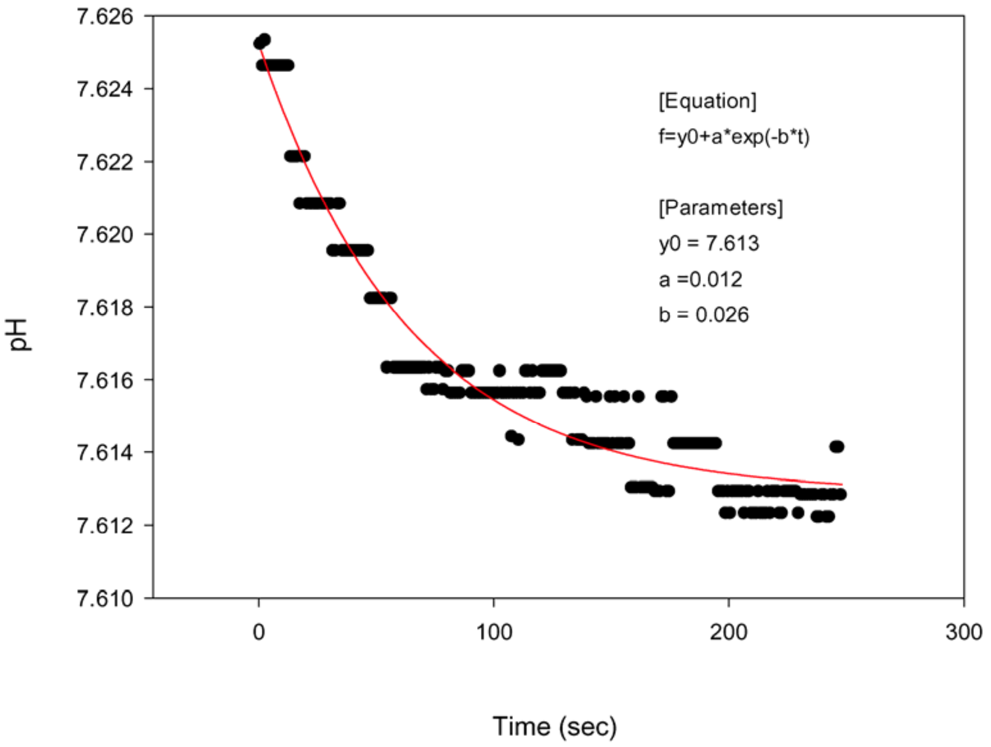
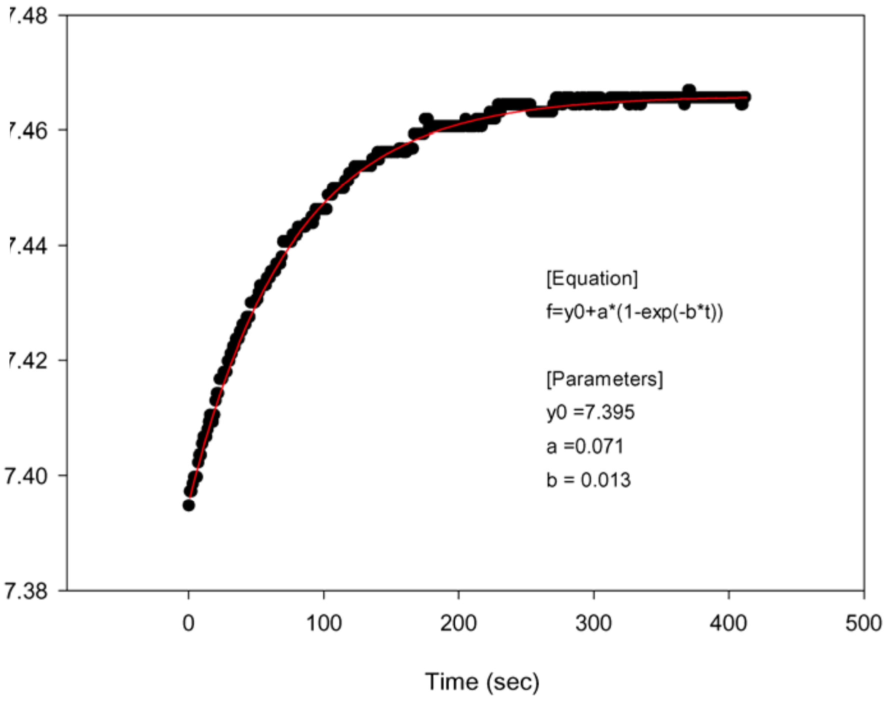


Fig. B



Ab Initio Molecular Orbital Calculations on the Water-Carbon Dioxide System. Reaction pathway for $H_2O + CO_2 \rightarrow H_2CO_3$. From Jonsson et al. 1978.

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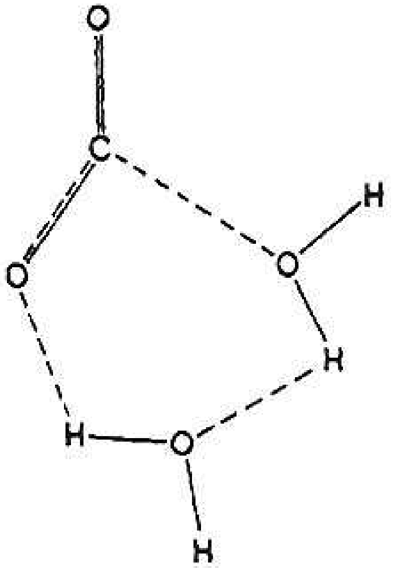

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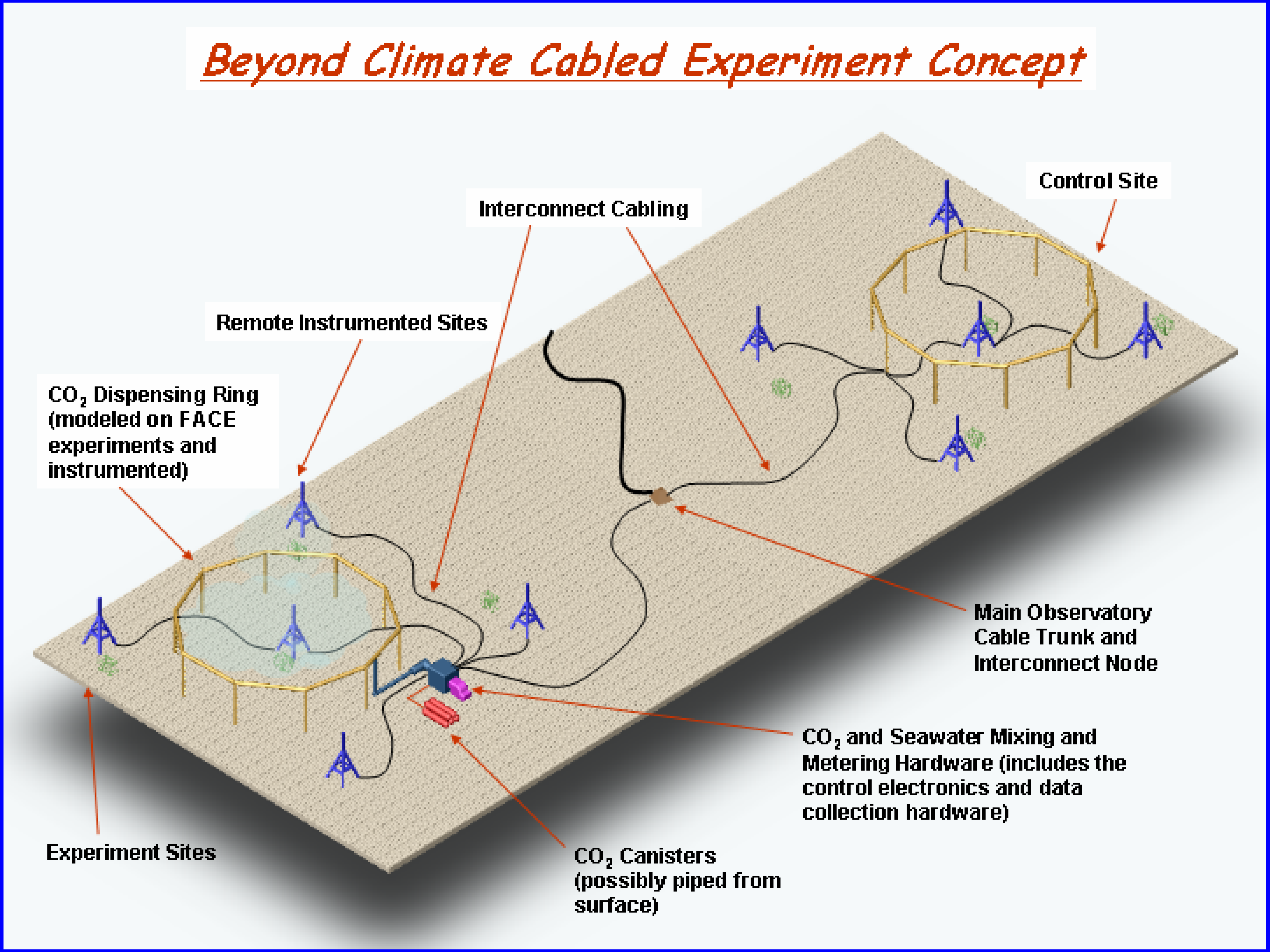
If we are to understand the science of a lower pH ocean we have to carry out predictive experiments. A concept sketch is shown here with supply of either acid or CO_2 to a set of experimental sites in much the same way that experiments are carried out on land. There are fundamental challenges in this.



Sunset over an ocean now > 0.1 pH units lower than pre-industrial. About 50% of the 500 billion tons of fossil fuel CO_2 now stored in the ocean is in the upper 250m.

With thanks to the Deutschen Physikalischen Gesellschaft for the kind invitation to speak