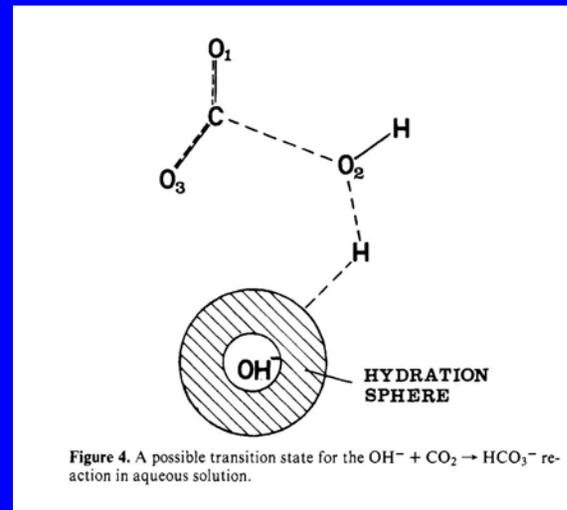


The Essential Science for Evaluating Direct Injection and the Emerging High CO₂ Ocean: Designing the Next Generation of Ocean CO₂ Experiments

Peter G. Brewer
Monterey Bay Aquarium Research Institute

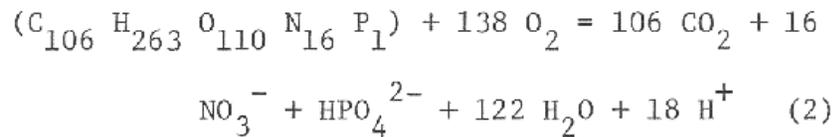


“The Ocean in a High CO₂ World”
SCOR-IOC
Paris
May 10 – 12, 2004

Direct Observation of the Oceanic CO₂ Increase – Brewer (1978)

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

For addition of CO₂ by respiration, the well-known relationship



holds. The change in alkalinity due to CaCO₃ dissolution ($\Delta \text{Alkalinity}_{\text{CaCO}_3}$) is then

$$\Delta \text{Alkalinity}_{\text{CaCO}_3} = \Delta \text{Alkalinity} + \Delta \text{NO}_3 \quad (3)$$

Thus the change in total CO₂ is given by (4)

$$\Delta \Sigma \text{CO}_2 = [\Delta \text{O}_2 \times 0.768] + [\Delta \text{Alkalinity}_{\text{CaCO}_3} \times 0.5]$$

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.

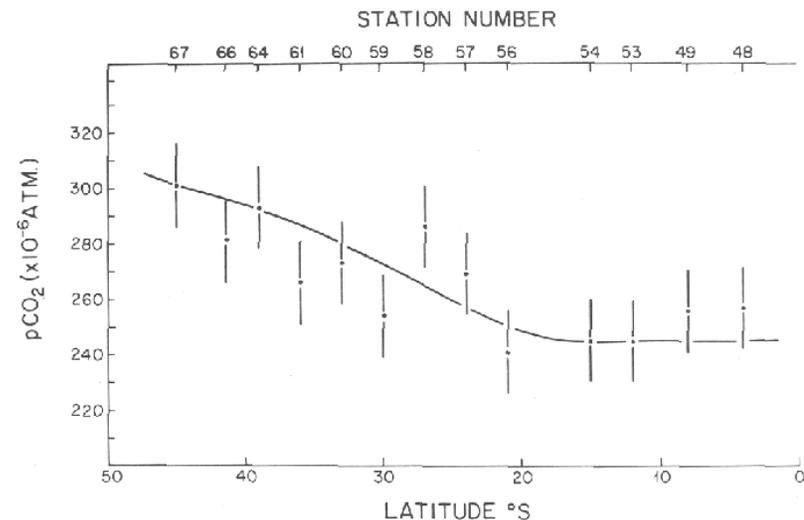
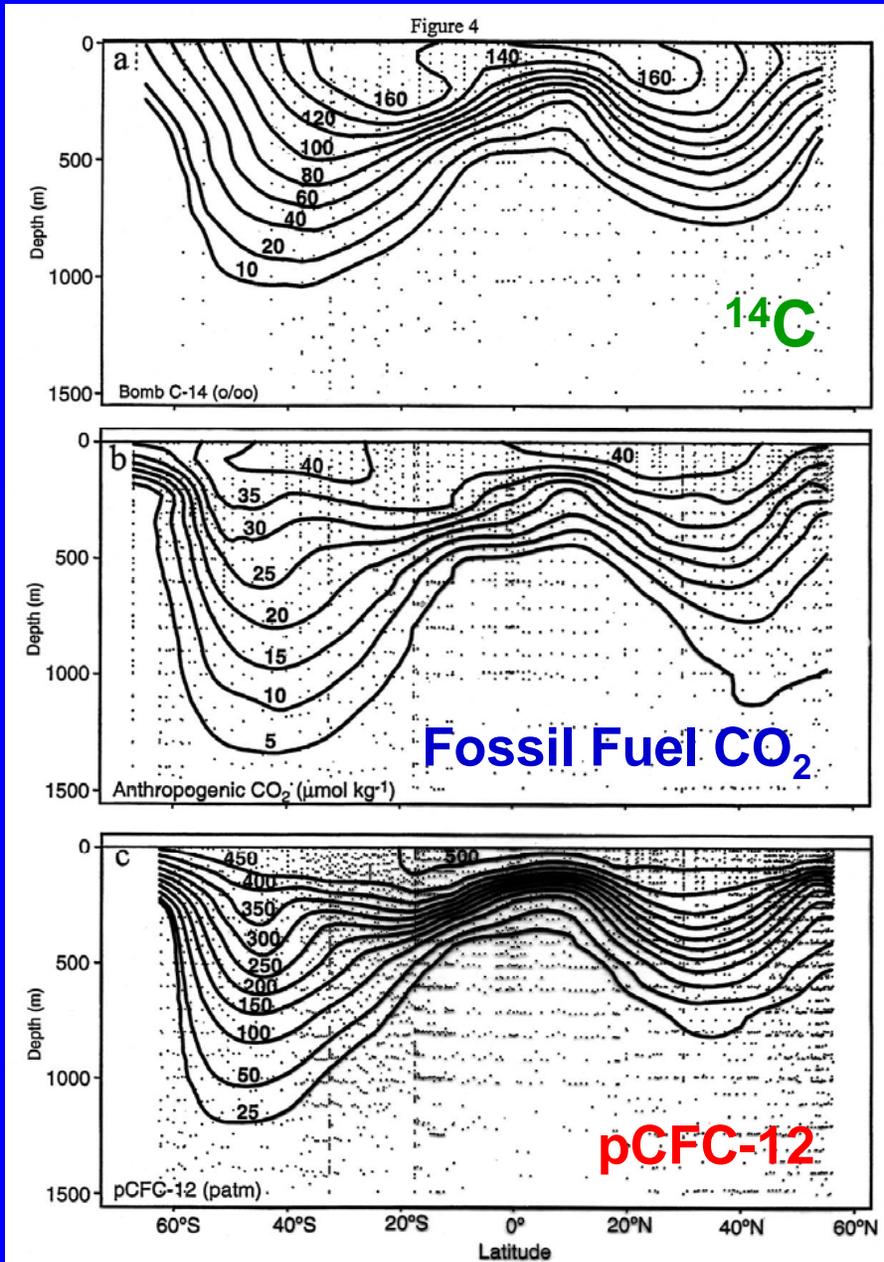


Fig. 2. The calculated initial pCO₂ of samples taken at the core of the salinity minimum of the Antarctic Intermediate Water in 1972.

Ocean CO₂ “Disposal” Today



From Sabine et al. 2002:

JGOFS/WOCE survey data. Pacific meridional section.

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

We have disposed of ~ 163 billion tons of CO₂ in Pacific Ocean waters.

The ocean now has taken up ~400 GT of fossil fuel CO₂.

Global surface ocean CO₂ disposal is now about 20-25 million tons per day.

The evolving chemistry of surface sea water under “Business as Usual”

Time	pCO₂	Total CO₂	pH	HCO₃⁻	CO₃²⁻	H₂CO₃
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

Under IPCC IS92A the pH of surface sea water drops by 0.4 pH units by 2100. CO₃⁼ in surface water drops by 55% from pre-industrial values. It will be hard to meet even these goals.

Fossil fuel CO₂ is now a major ion of sea water.

From Brewer, 1997

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

IPCC 1990 “Business As Usual” Assumptions

- *In 100 years renewable and nuclear technologies will provide more than 75% of all electric power, compared to 24% in 1990.*
- *Non-carbon technologies (including solar and wind) are assumed to grow to about twice the size of the entire global energy system in 1990.*
- *Energy consumed per unit of economic activity declines to 1/3 of 1990 levels.*
- These assumptions pose huge technical challenges

From Wigley et al. (1996)

Emission trajectories required to achieve stabilization of atmospheric CO₂ levels at various values incorporating “best” economic choices.

In order to achieve stabilization at 550 ppmv departures from current trends of about 3.67 billion tons of CO₂ per year are required by 2025, and about 14.7 billion tons per year by 2050.

This may be achieved by conservation, substitution, or sequestration strategies.

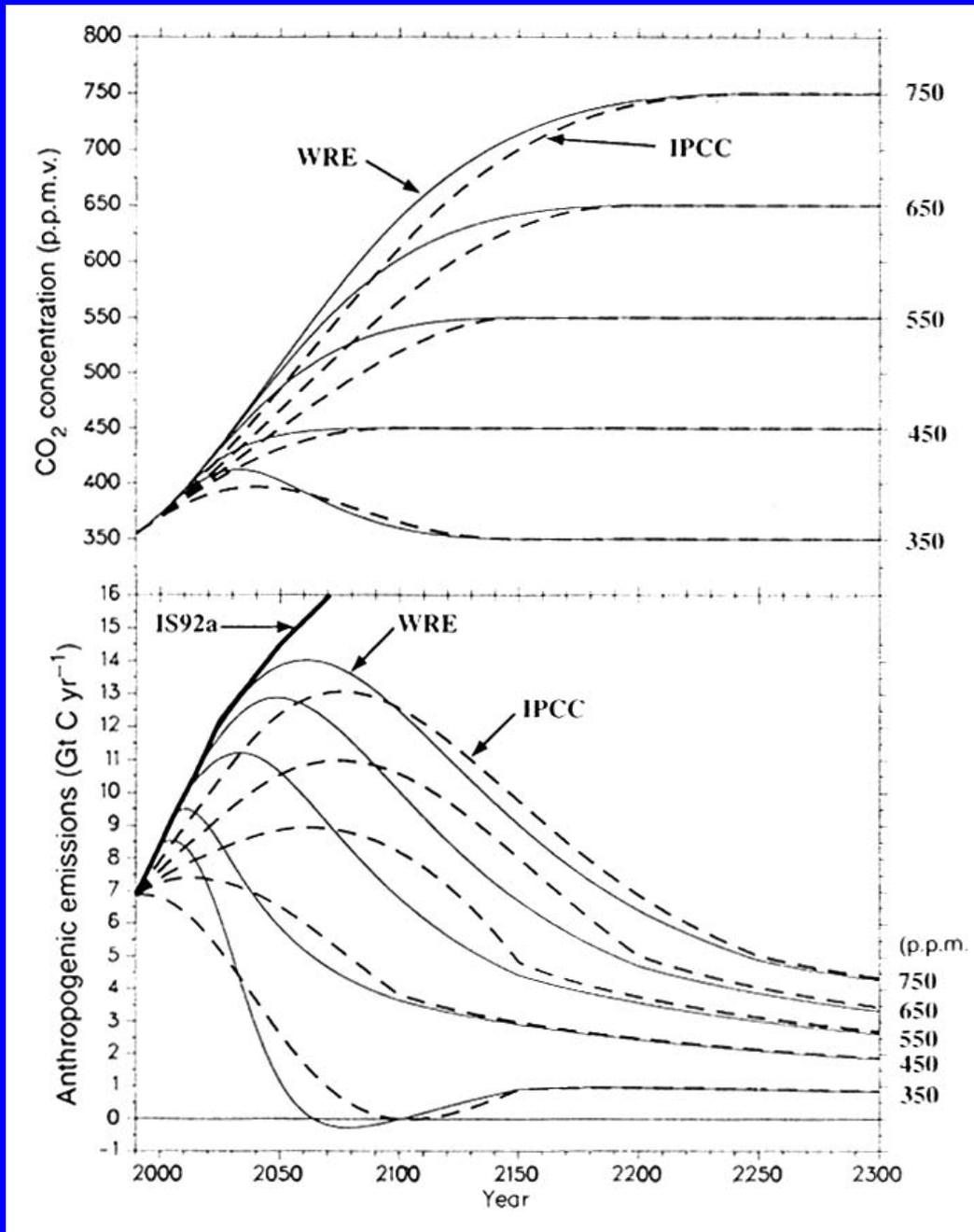
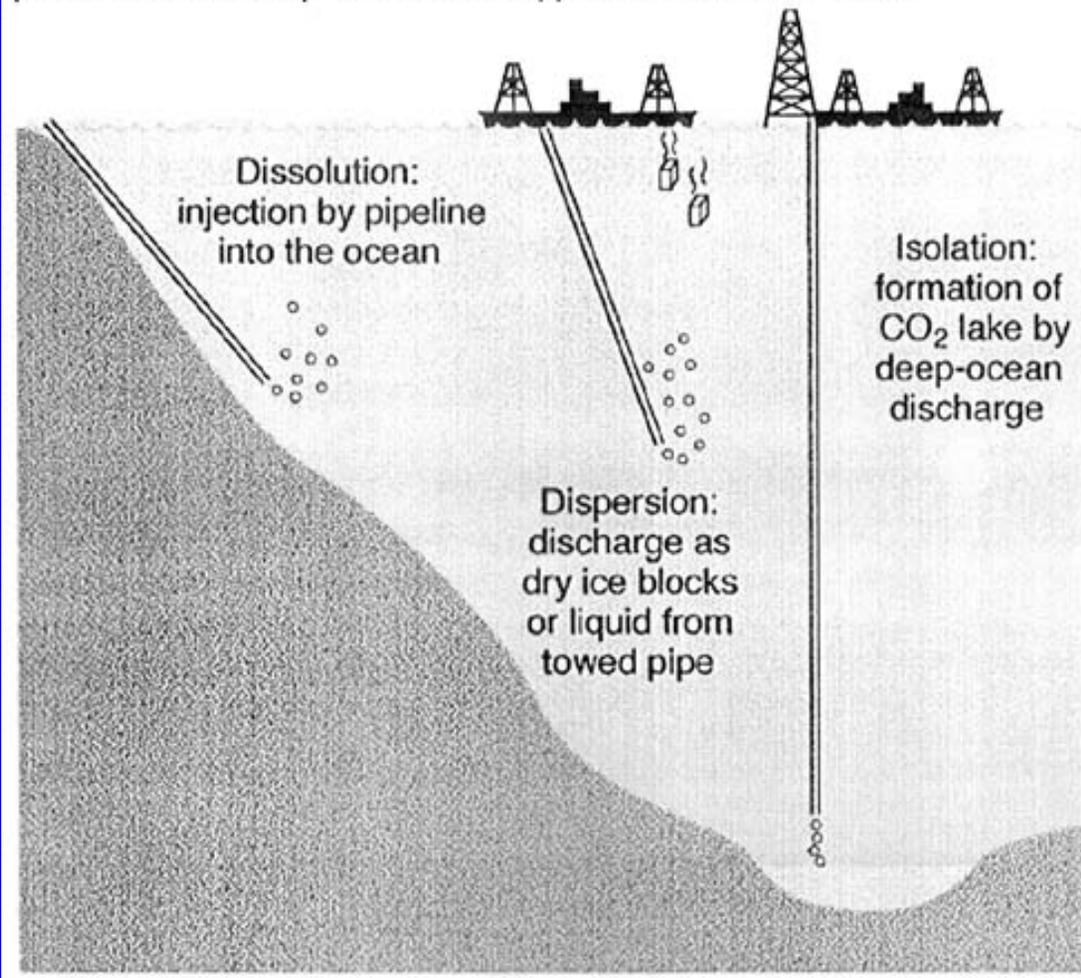


FIGURE 1

Options for direct ocean disposal of CO₂

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 CO₂ 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 CO₂ 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 CO₂ disposal technologies.

The policy area is cloudy.

An early CO₂ sequestration experiment (Brewer et al. 1999)



There are few beakers on the normal ocean floor! – yet we continue to use contained CO₂ 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 CO₂ in much the same way as is done on land.

The complex self-generating fluid dynamics of this experiment 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.

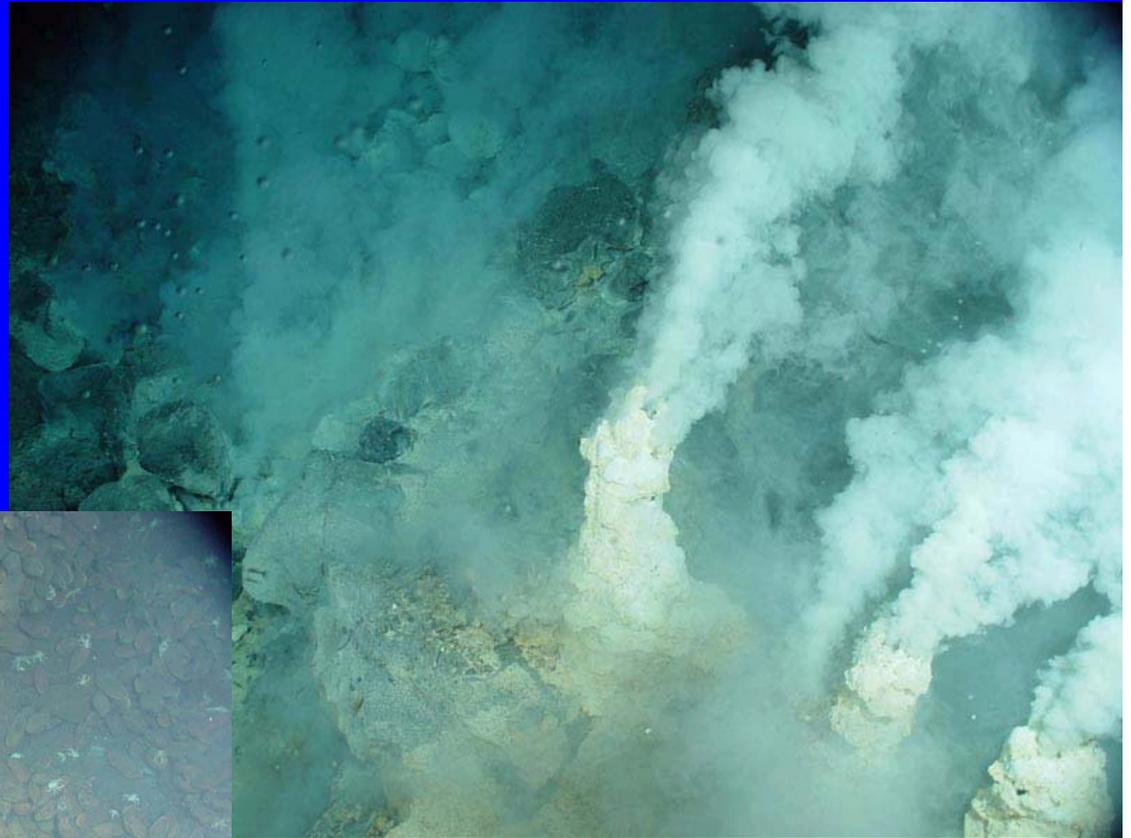
Reality Check

All nations, whether maritime or landlocked, dispose of CO₂ in the ocean. We employ the euphemism “natural uptake” to describe this strategy.

- *Surface ocean CO₂ uptake/disposal is now \cong 25 million tons CO₂/day*
- *Consider 1% of this as a target for direct injection*
- *This equals 250,000 tons per day*
- *This could be achieved by five 50,000 ton LCO₂ tankers loads per day*
- *With a 4-5 day turn around this would require 20-25 such tankers*
- *The costs, independent of the dominant CO₂ capture costs, would be high, and the project controversial. It could not happen for decades.*
- **But even if this was done, then 99% of the environmental concern over ocean pH/CO₂ burdens would logically be directed at the enormous and rapidly growing upper ocean signal.**

Natural Deep Ocean CO₂ Sources

A newly discovered liquid CO₂ hydrothermal vent at 1600m depth, Eifuku volcano Marianas Arc by the NOAA team



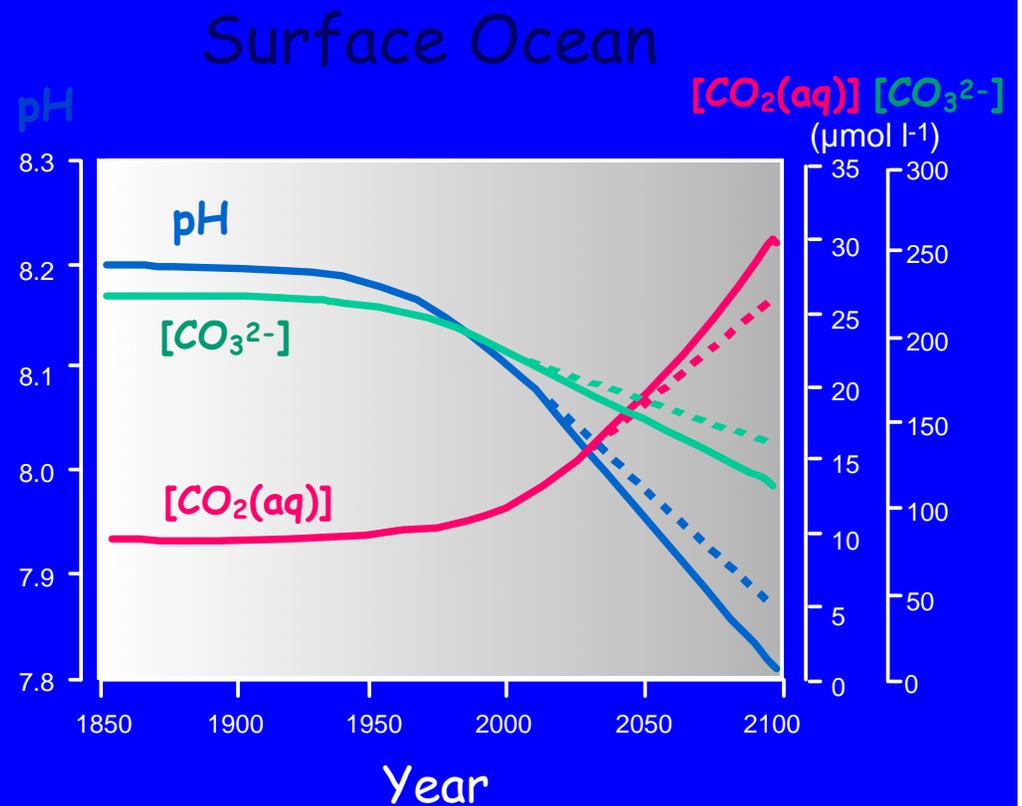
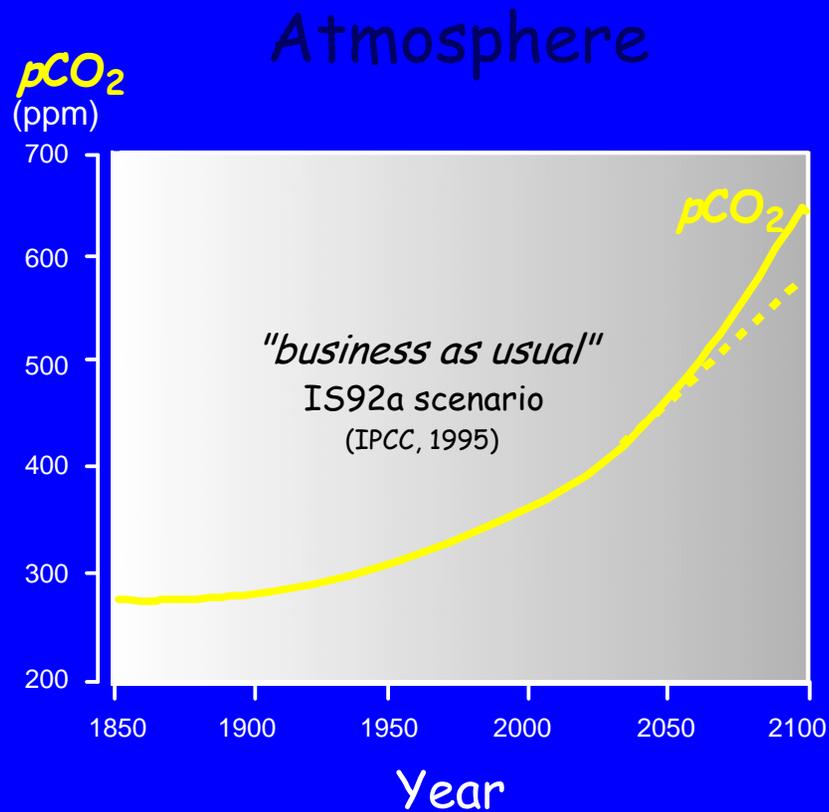
Extensive mussel beds are found in close contact with the CO₂ source.

Large droplets of liquid CO₂ coated with hydrate emerge from the sea floor at Eifuku. These are identical in appearance to some of the controlled experiments carried out by the MBARI team.

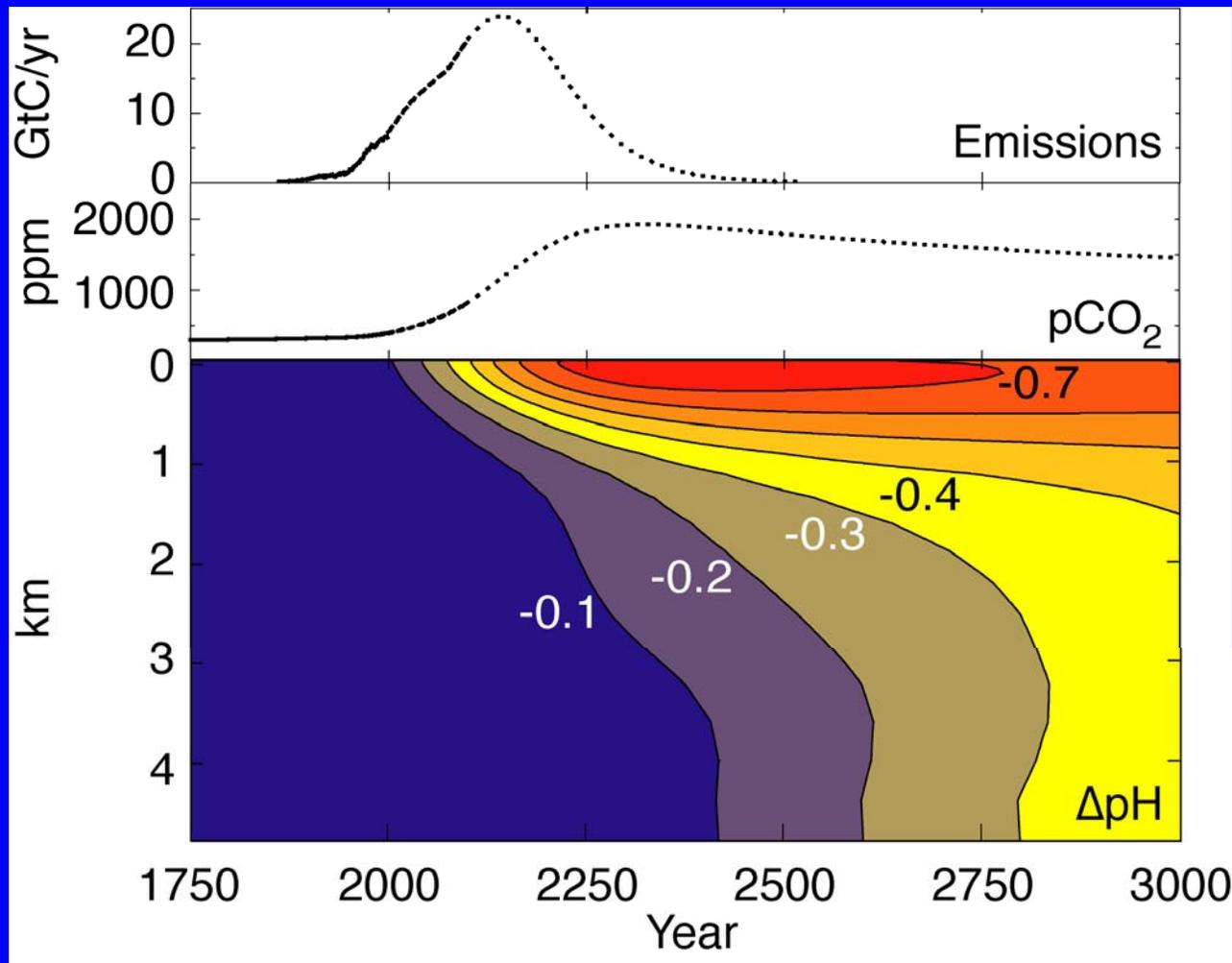


While natural venting of liquid and gaseous CO₂ can provide elegant scientific insights, this will not substitute for carrying out controlled experiments on a wide variety of biogeochemical systems.

Changes in seawater carbonate chemistry due to atmospheric CO_2 increase



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



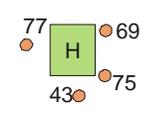
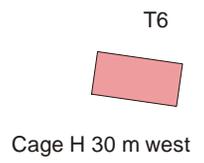
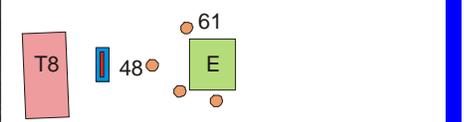
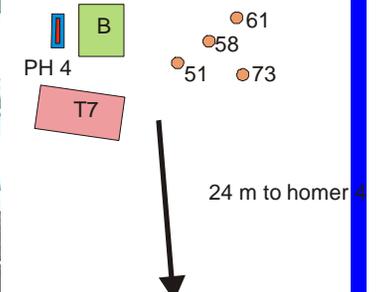
To a great degree these changes are inevitable for an energy rich society. While climate change has uncertainty, these geochemical changes are highly predictable. Only the time scale, and thus mixing scale length are really under debate.

From: Caldeira and Wickett (2003)

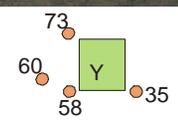
Reality Check

- *If ocean ecosystems are sensitive to pH changes of the order 0.3 – 0.7 pH units then we face a near inescapable problem – ocean chemistry WILL change under any energy scenario.*
- *Plans for creating large nuclear/wind/solar energy components are already built into IPCC projections.*
- *Such plans do not eliminate fossil fuel use/atmospheric release, they simply extend the time scale.*
- *This may help ameliorate climate change by giving the ocean more time to absorb the CO₂, and extend the mixing length scale*
- *In the long run some 85% of the fossil fuel reserves will be transferred to the ocean.*
- *If we use geologic disposal then we can reduce this burden, but the costs are high – even sequestration of 10% of known reserves would impose enormous economic costs, and pose environmental questions for the land.*

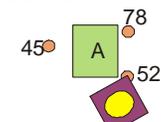
CO2 release exp. II – Oct. – Dec. 2001



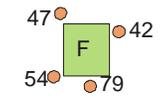
Homer 49 = 40 m



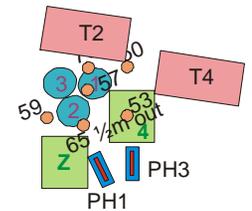
At1



Time lapse camera
Homer 33

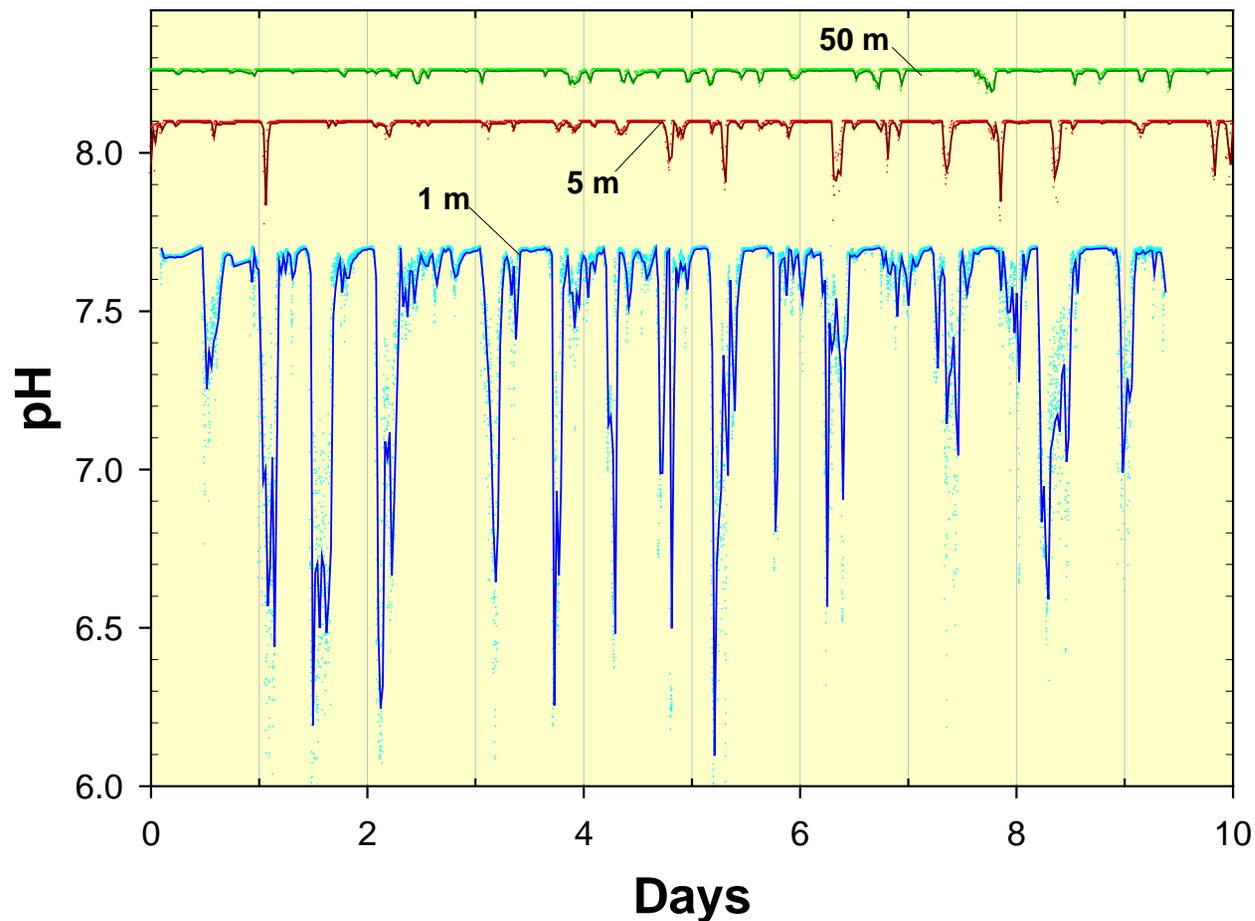


Homer

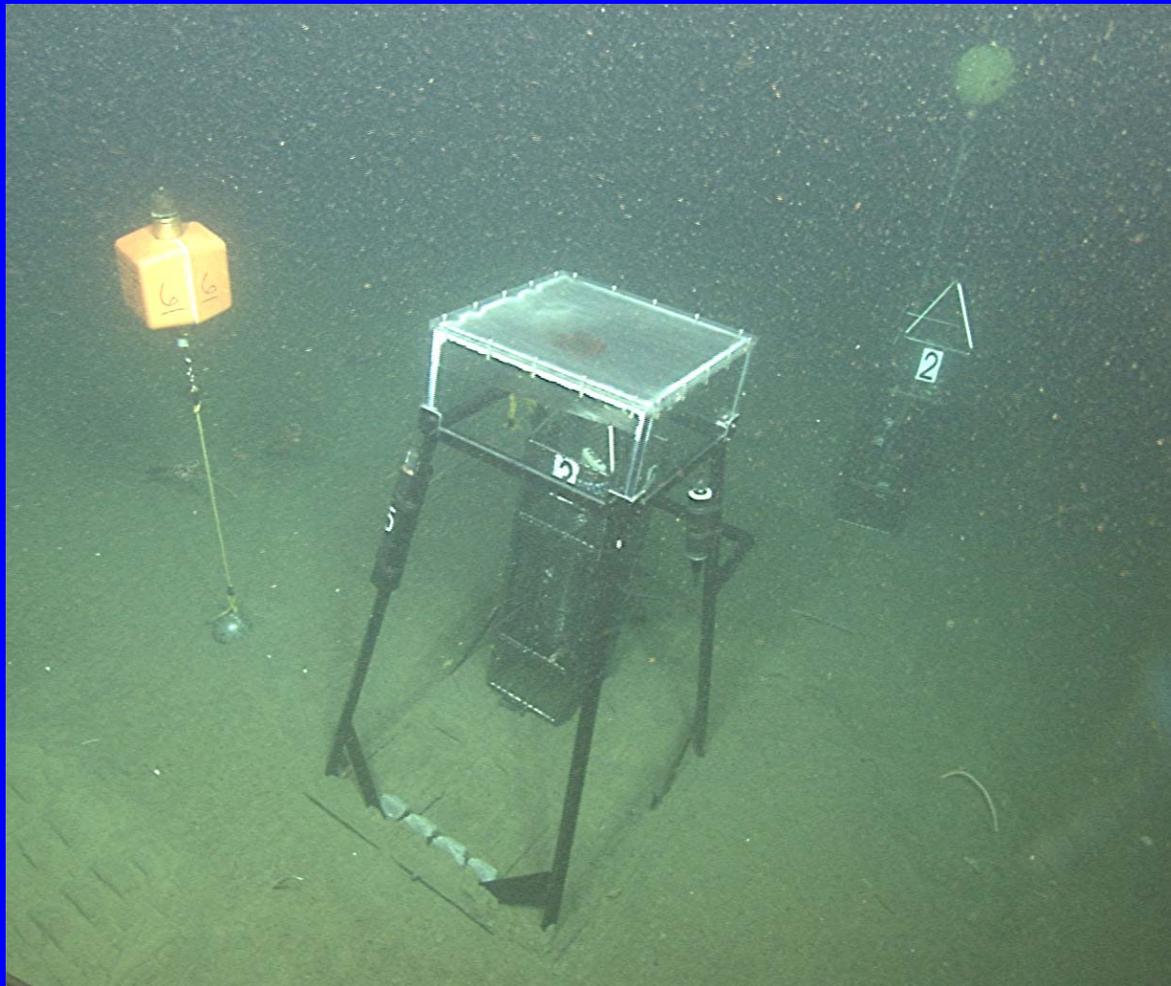


Data fragment over 10 days from recording pH sensors at 1, 5, and 50m distance from the central CO₂ corral site. The instrument drift has been removed, and the baseline data normalized to true ocean background values.

From Barry et al. (2003)



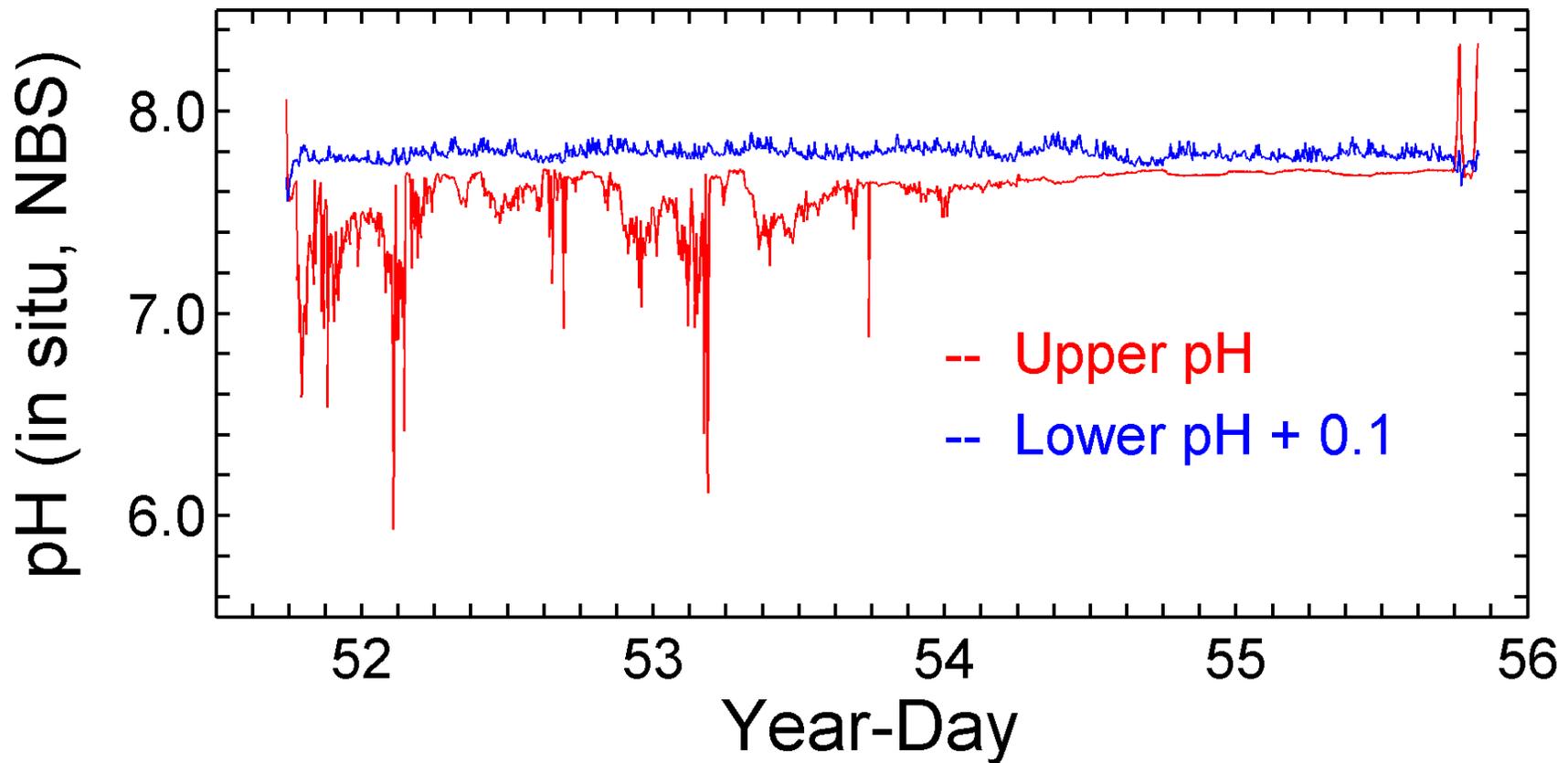
View of the OACE1 experiment. The frame is 120cm high, the base of the box is 103cm above the sea floor. The box is 47 cm square, with walls 23 cm high. The pH-CTD frame is seen immediately behind the frame; a second set of sensors is 2 m away. Depth = 650m. From Brewer et al. In Press.



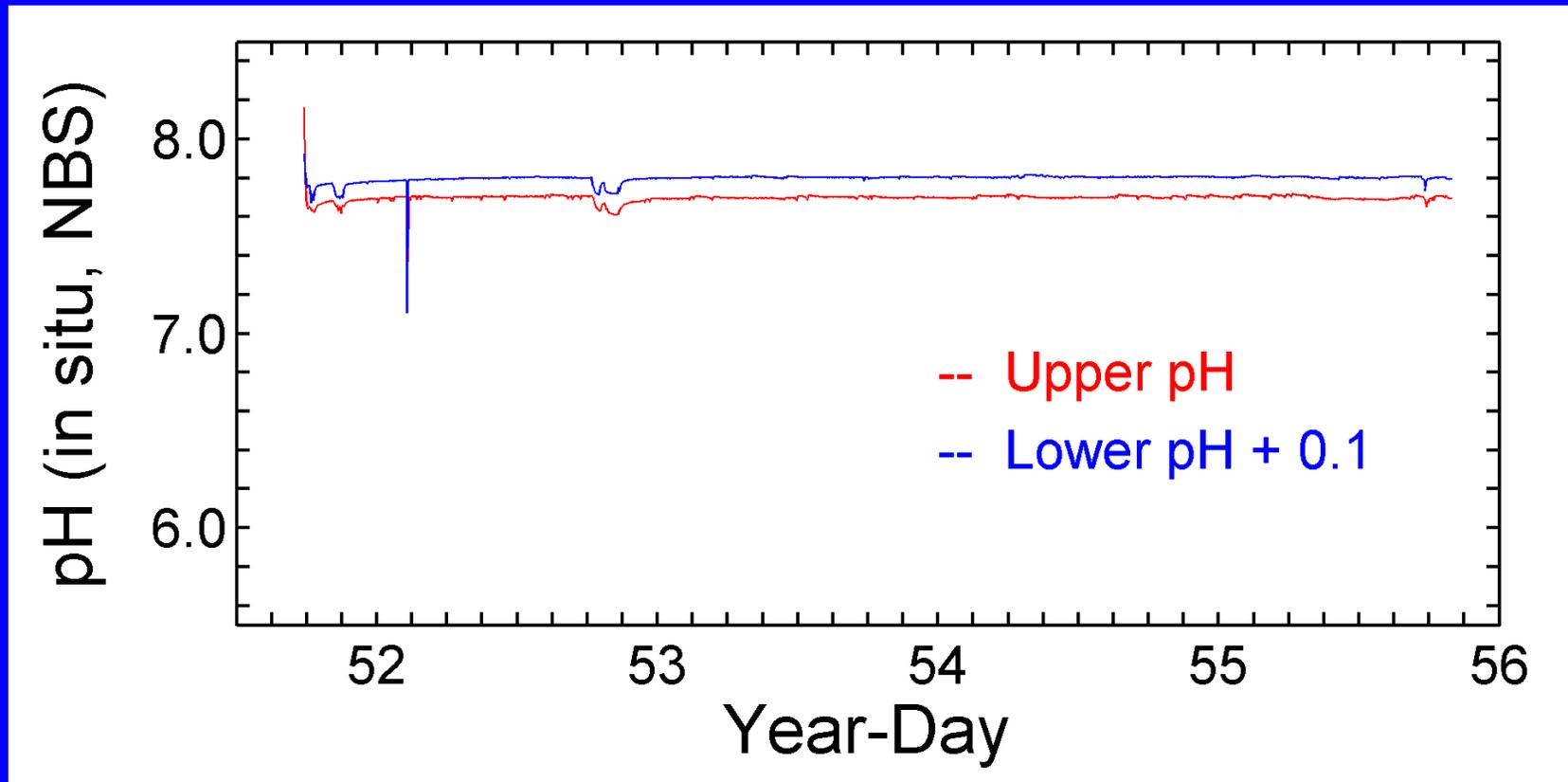
The experiment was designed to test the signature of the dense low pH plume from the CO₂ pool.

- A sinking plume?*
- CO₂-H₂O reaction rates?*
- Sensor stability?*
- pH sensitive dye?*
- Effect of ocean currents on the interface?*

Some results from OACE 1 – pH signals were only detected very close to the source, the plume was not sufficiently dense to sink far, and the tidal flow caused strong eddies within the box exciting wavelets at the CO₂–water interface. The spiky pH signals result from this non-linear eddy activity. The experiment was carried out in the MBNMS with a NOAA permit, and was designed for technique development.

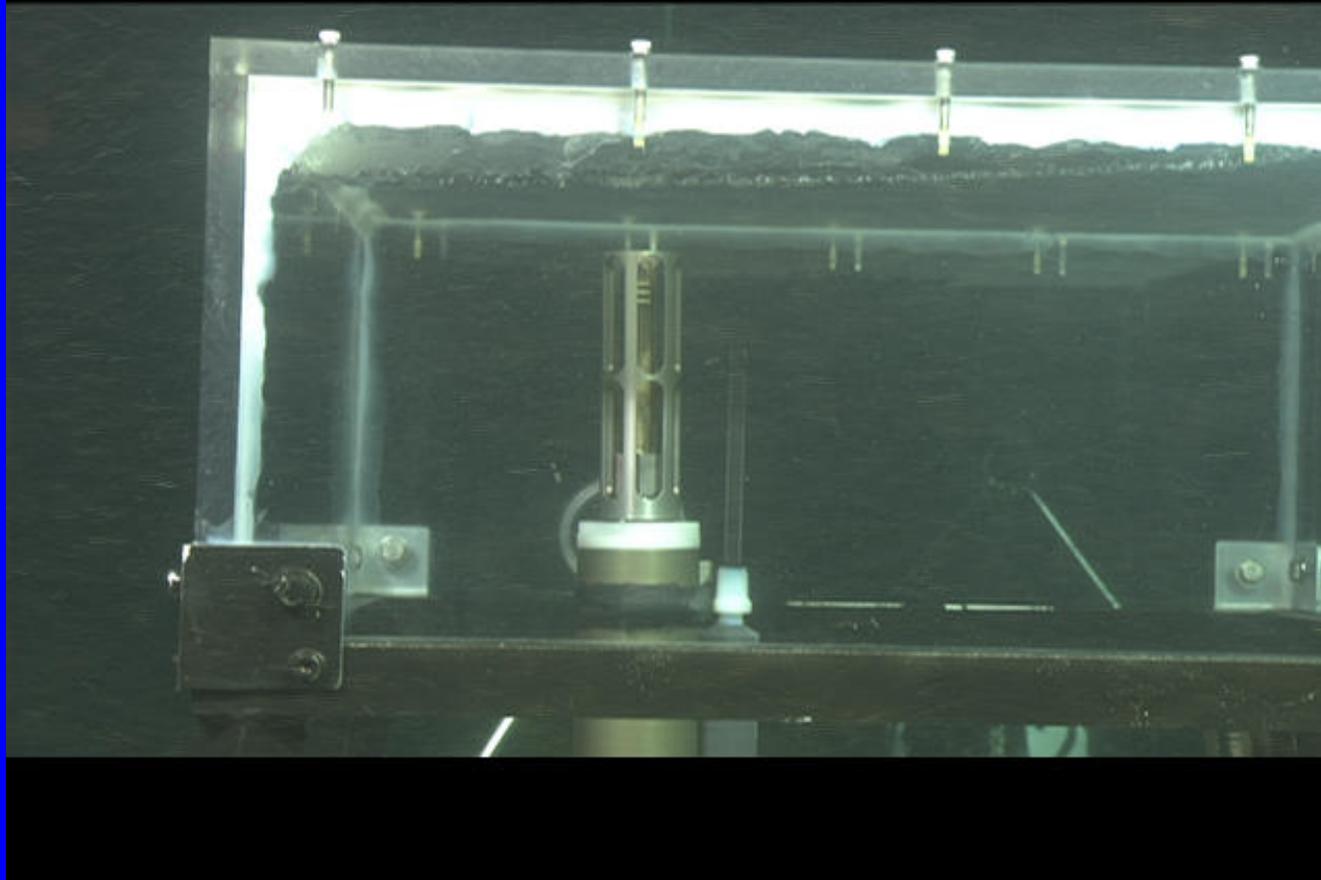


The pH recorded about 2m distant from the inverted box. Only very small signals are seen. The events seen on Day 53 were from ROV landing and disturbing a cloud of pore water rich in CO₂.

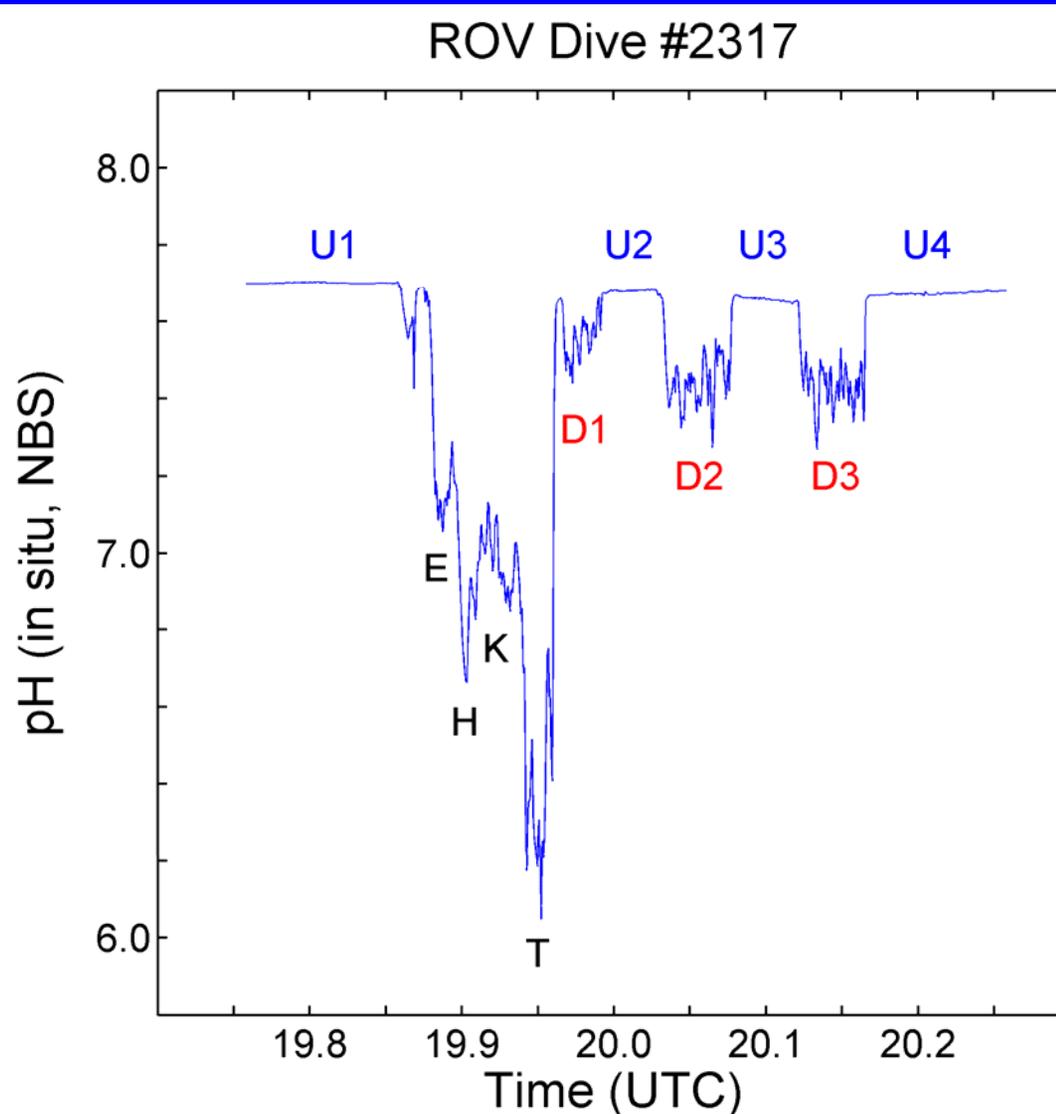


The erratic nature of the flow field, and eddies induced by the structure make plume sensing difficult with these small scale systems – by moving the electrode around the source we can measure the signal strength, noise levels, boundary layer influence etc. Here the inverted pH electrode is held close to the CO₂-water interface.

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Copyright 2003 Monterey Bay Aquarium Research Institute  
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Results from pH sensing of the plume from the OACE 1 experiment:
Direct electrode placement.

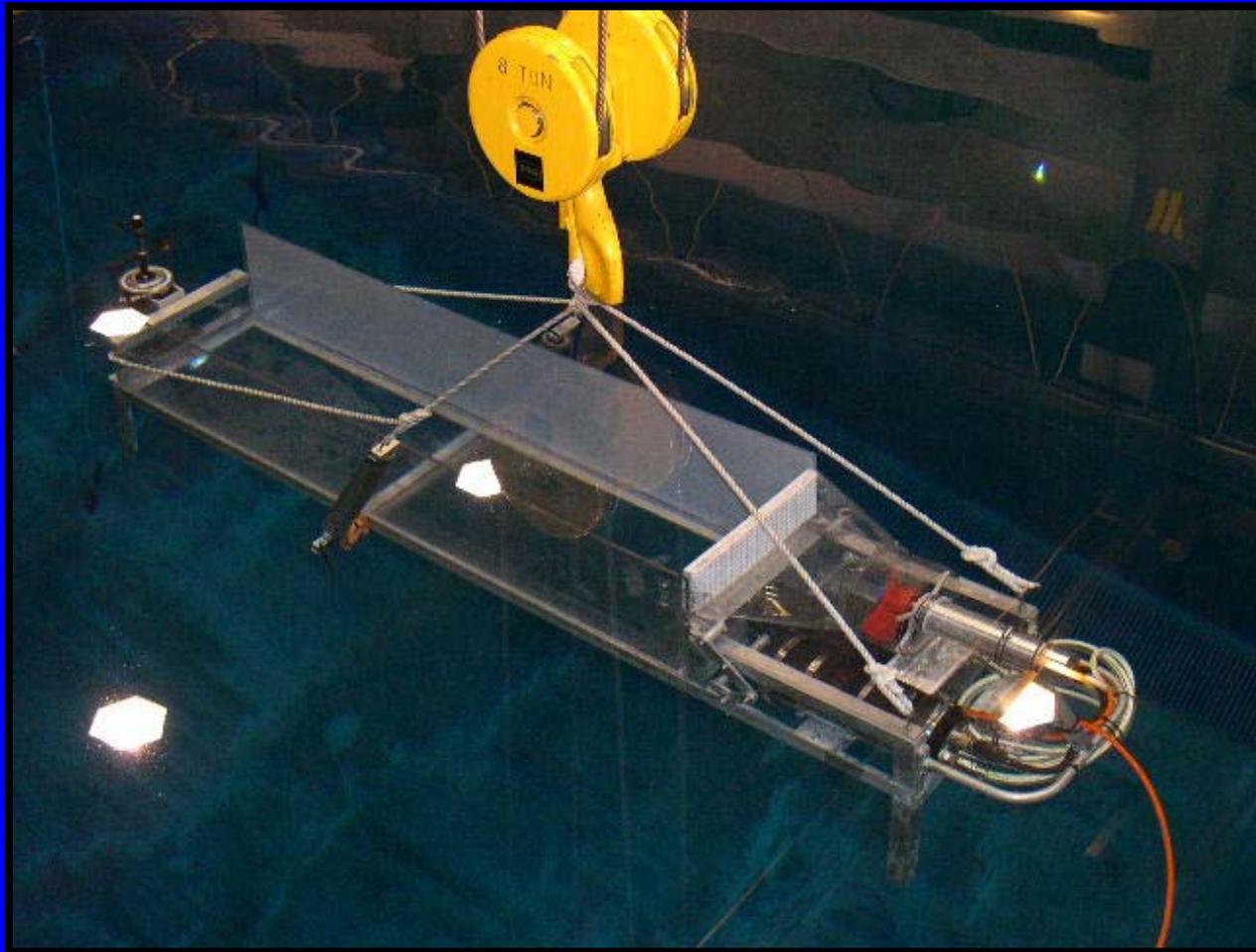


pH values were calibrated and reported on the NBS scale. The probe was placed upstream, inside the box, and downstream.

- *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 $\cong 6.0$*

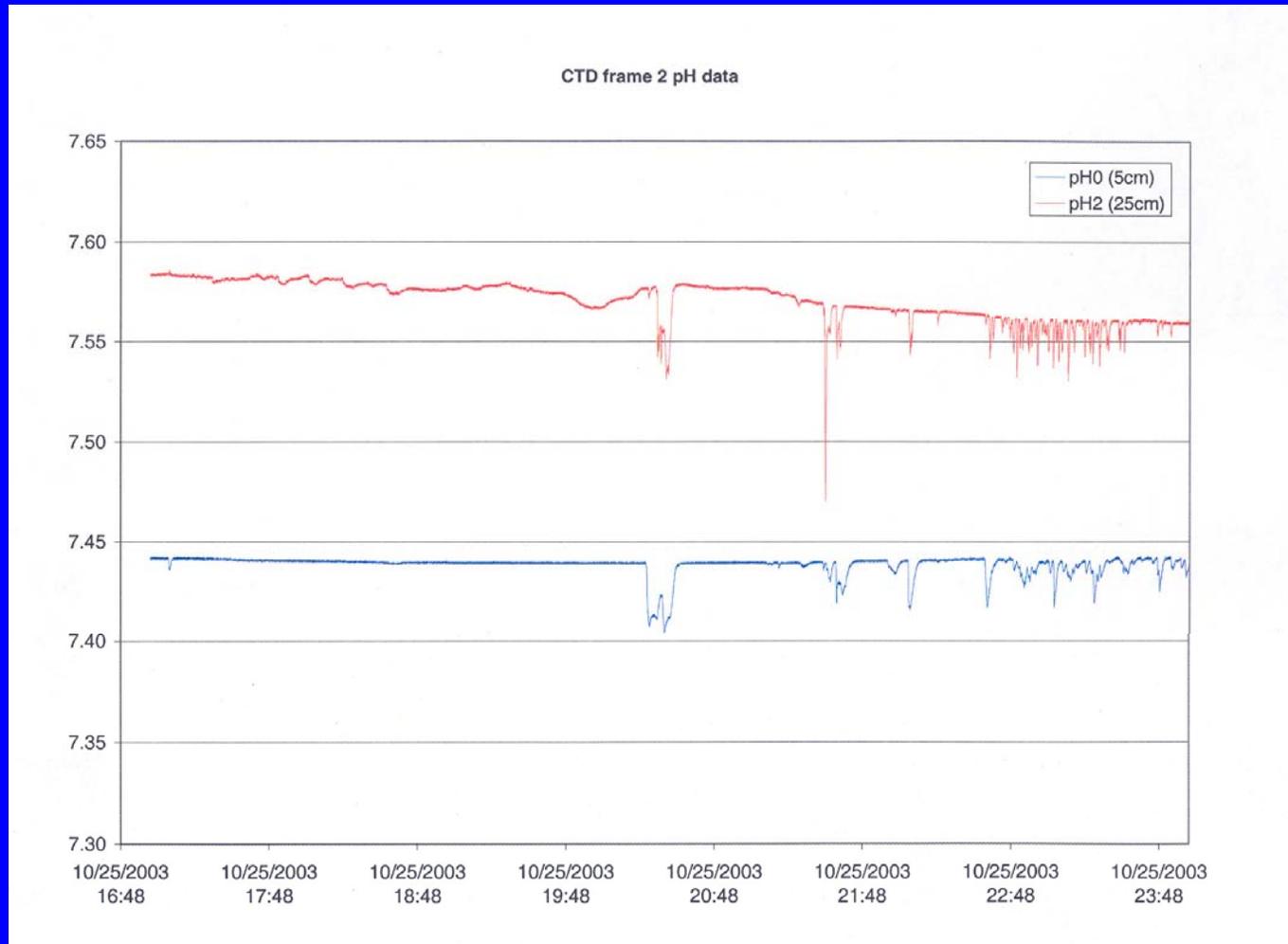
Creation of a controlled plume of high CO₂ – low pH water

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 CO₂. By activating the thruster we could induce gravity waves on the liquid surface and force a directed plume for sensor (pH,CTD) detection downstream.

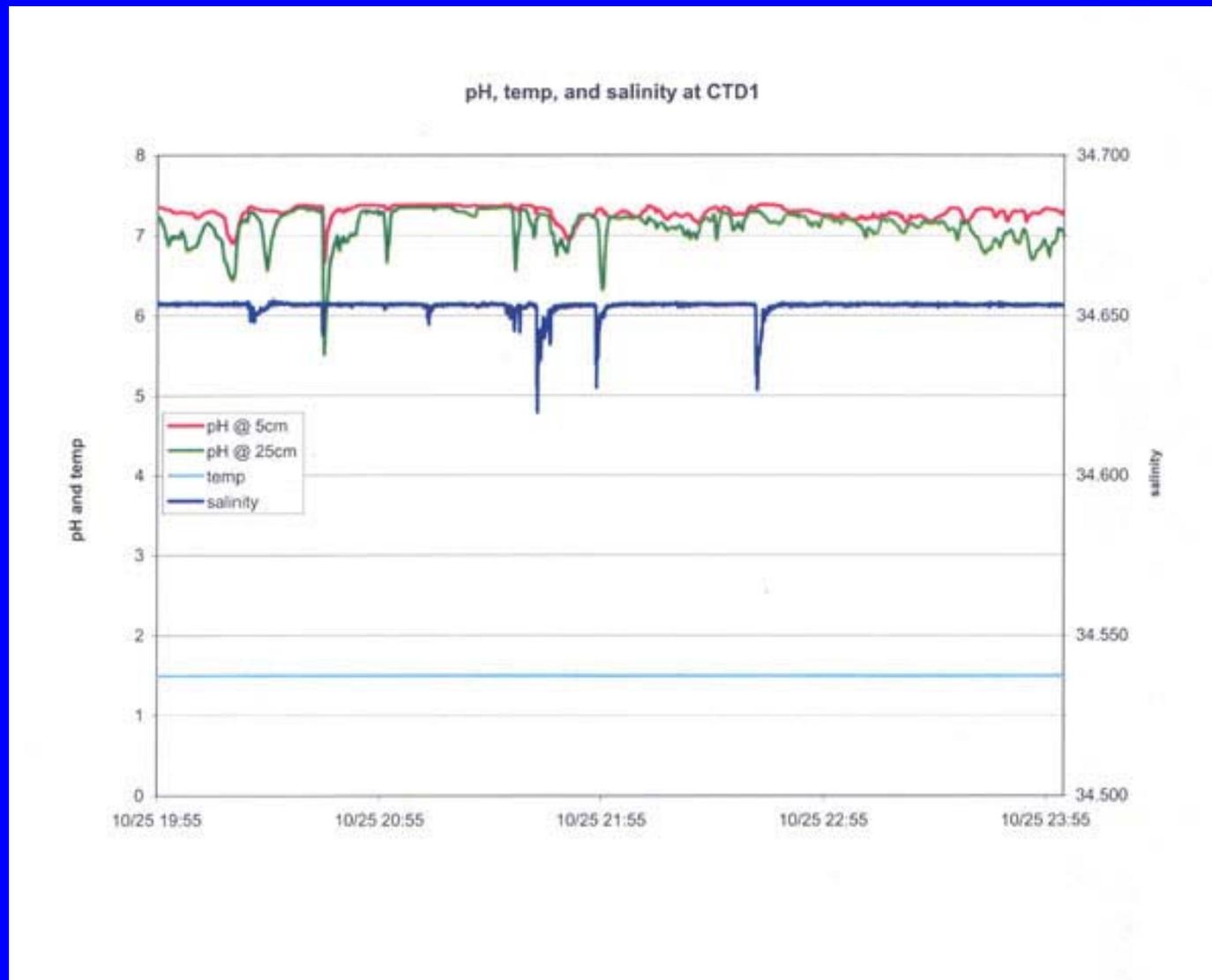


DVD of 4 km CO₂ Plume Experiment

Data fragment from the 4 km CO₂ plume experiment, showing the pH sensor responses to various forced flows over the liquid CO₂ surface. Very clear and coherent signals are seen, and the duration and intensity is controllable. But the influence of local currents steers the plume, and a single static sensor unit records this effect.



Data fragment from the plume sensing experiment. The low pH signal is recorded by the CTD due to the conductivity change from increased HCO_3^- ion. For pH changes of >0.1 the effect is readily detectable (Brewer & Bradshaw, 1975). Offsets are due to small differences in sensor placement in the plume.



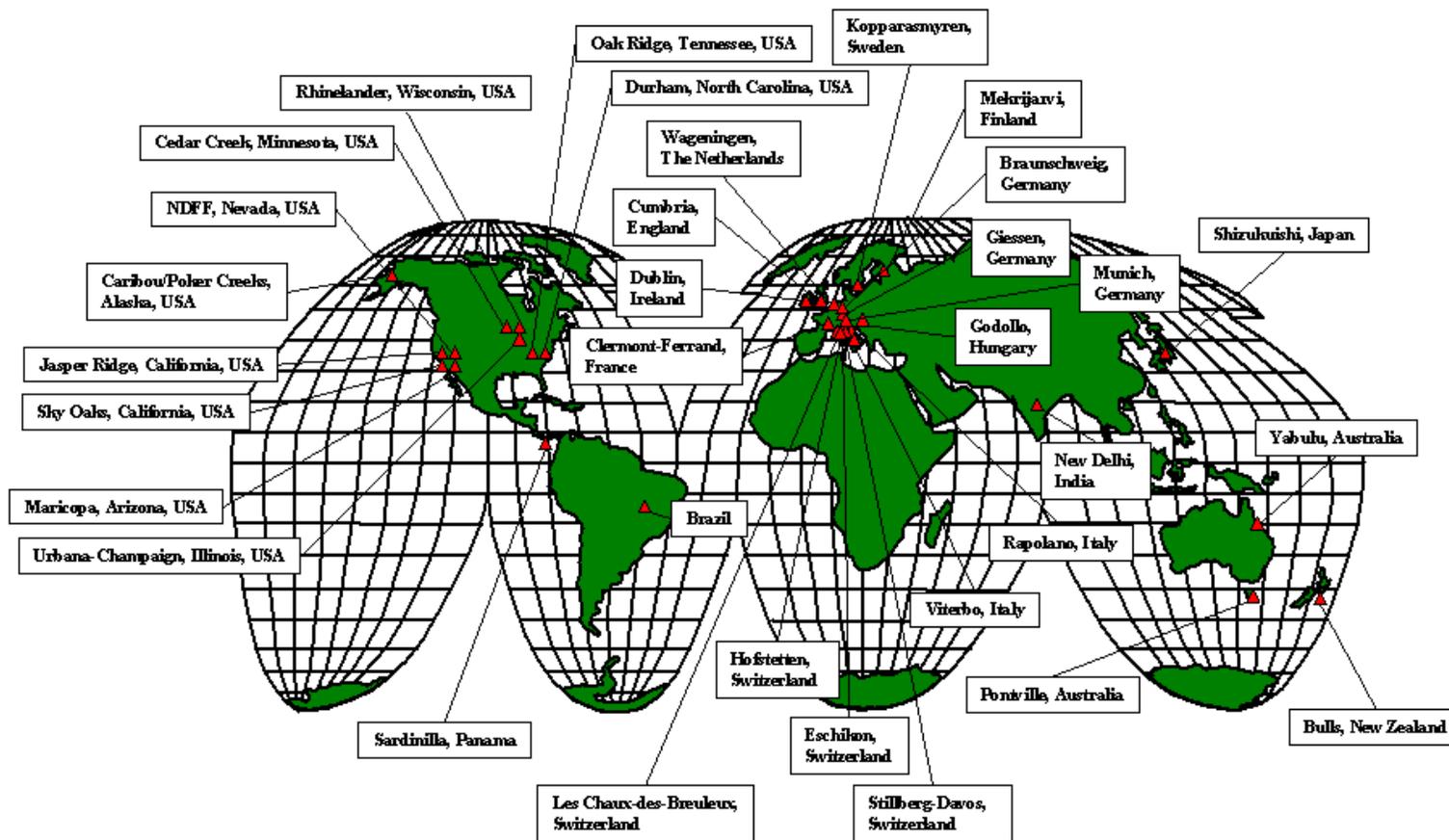
Large Scale CO₂ Enrichment Experiments on
Land
FACE (Free Air CO₂ Enrichment)



FACE experimental site in a 13 year old 14m high Loblolly Pine plantation in North Carolina. The rings are 30m diameter. There are 3 experimental rings and 3 blanks. The CO₂ concentration was enriched by 200ppm over modern air (~560 ppm). The experiment ran for 2 years +. The result was a 26% increase in productivity, but cautions were given that this may not be sustainable or typical.

From DeLucia et al. (1999)

FACE Experimental Sites – Why are there no ocean CO₂ sites?



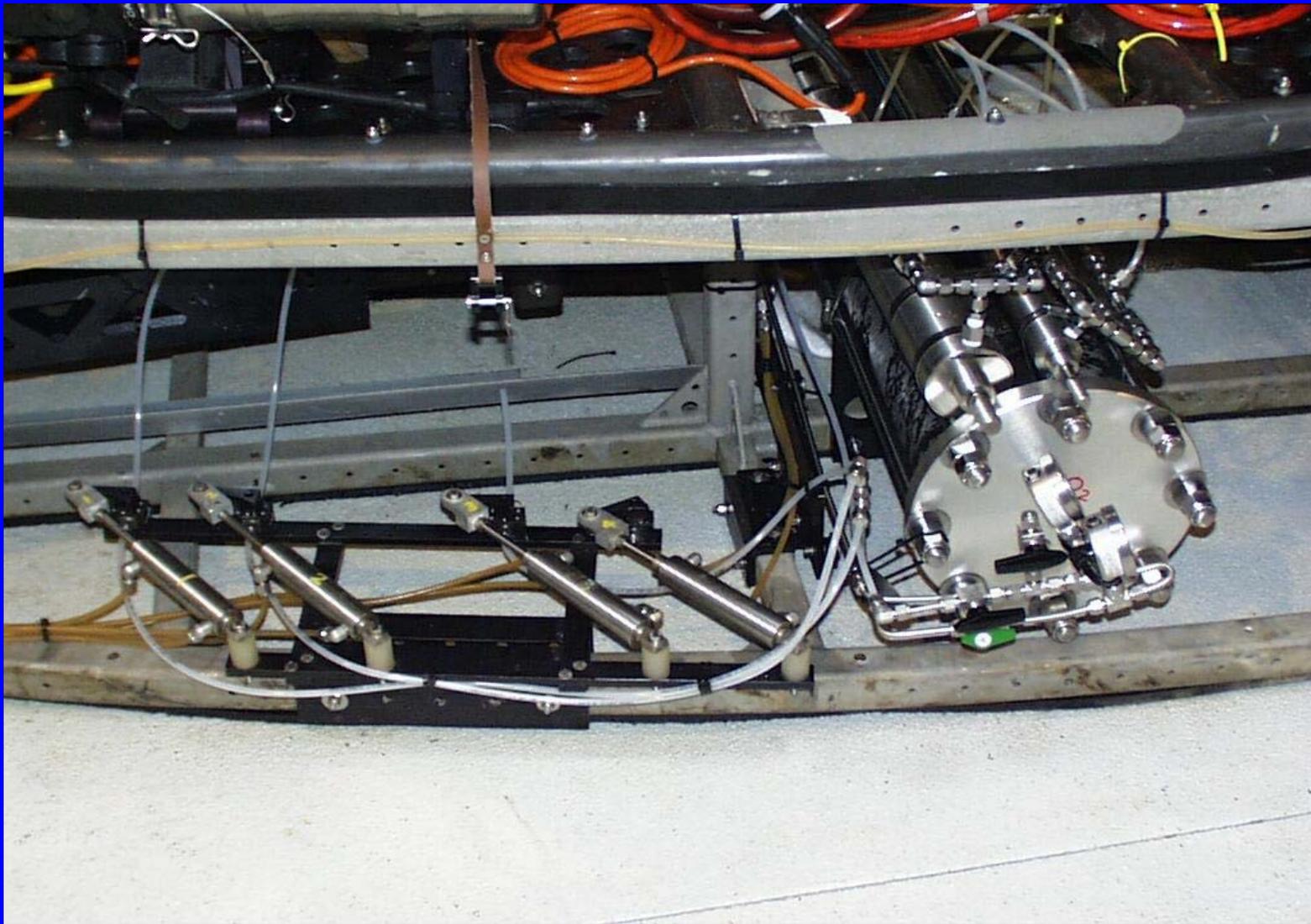
FACE CO₂ Delivery Engineering



Food grade, liquefied CO₂ is delivered by truck and transferred to an insulated Receiving Tank. Pressure is kept at 1725 kPa. CO₂ is piped through 5cm I.D. metal pipes to a pressure regulator, and pressure dropped to 140 kPa. CO₂ then flows through plastic pipe to the vertical pipes. Delivery rates vary from 0 to 1550 kg/hr.

Technique Development:

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



The FACE system in Wisconsin as an example of a CO₂ 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.



Experimental challenges lie ahead that will require sophisticated Engineer-Scientist interaction.

View of a FACE Site Showing Piping, Valves, and Sensors



The fragility and complexity of such an array would pose problems in the ocean where system servicing would be carried out by ROVs. We will need to create robust systems for ocean survival.

Valving, Feed-back, Mixing, and Control?

This is far easier with acid than with CO₂ itself, although above the hydrate phase boundary CO₂ is quite possible.

Sensor stability?

Deterioration of glass electrodes can occur from prolonged use due to the leaching of Li⁺ ions that provide the conducting path, thus leaving a hydrated and Li-depleted skin through which diffusion must occur.

Longevity of the reference electrode?

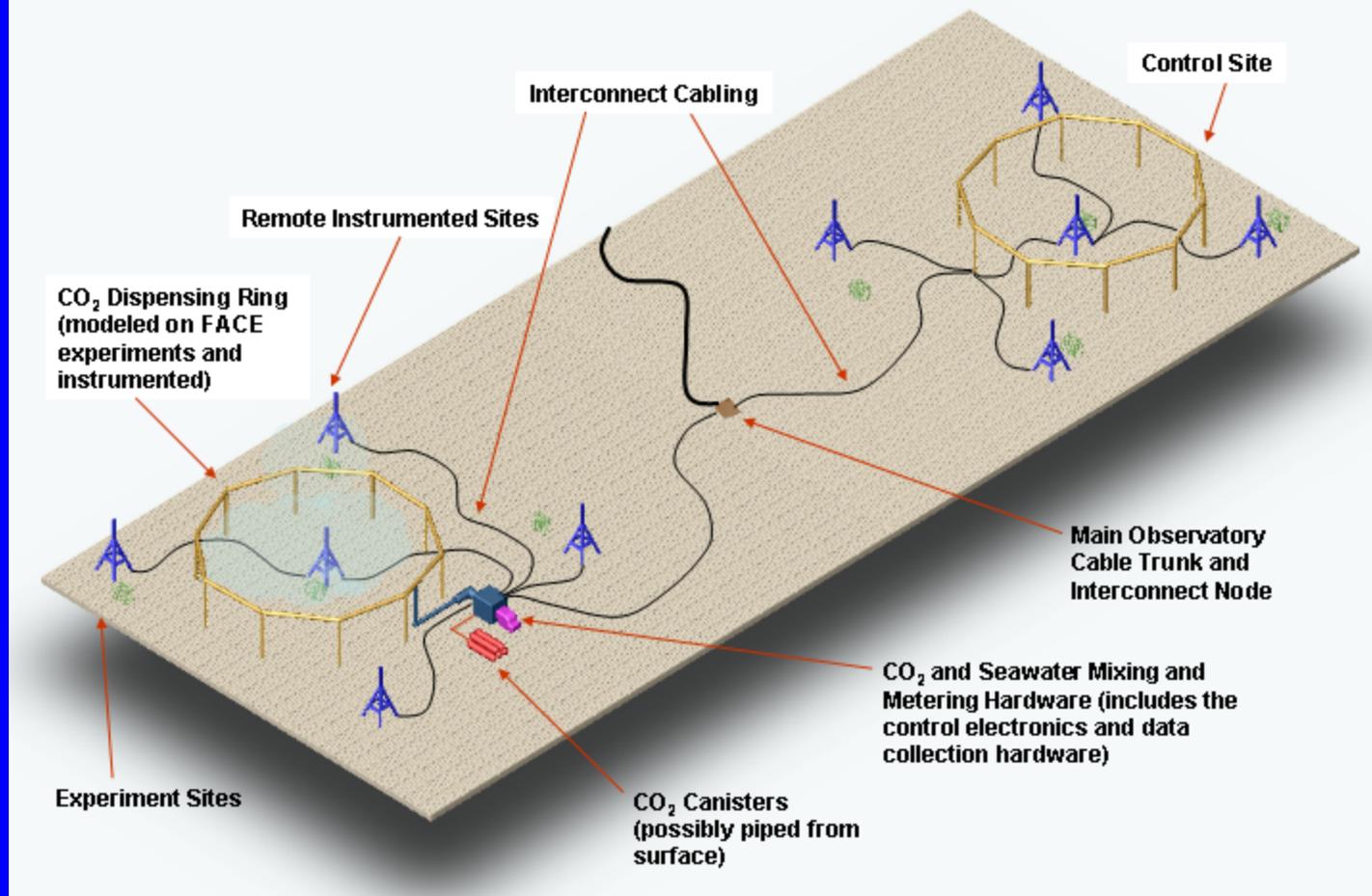
The slow leakage of KCl typically used to provide the salt bridge is affected by pressure changes, and the reservoir will become depleted.

Sampling?

Non-invasive signal/data recovery must be used as much as possible.

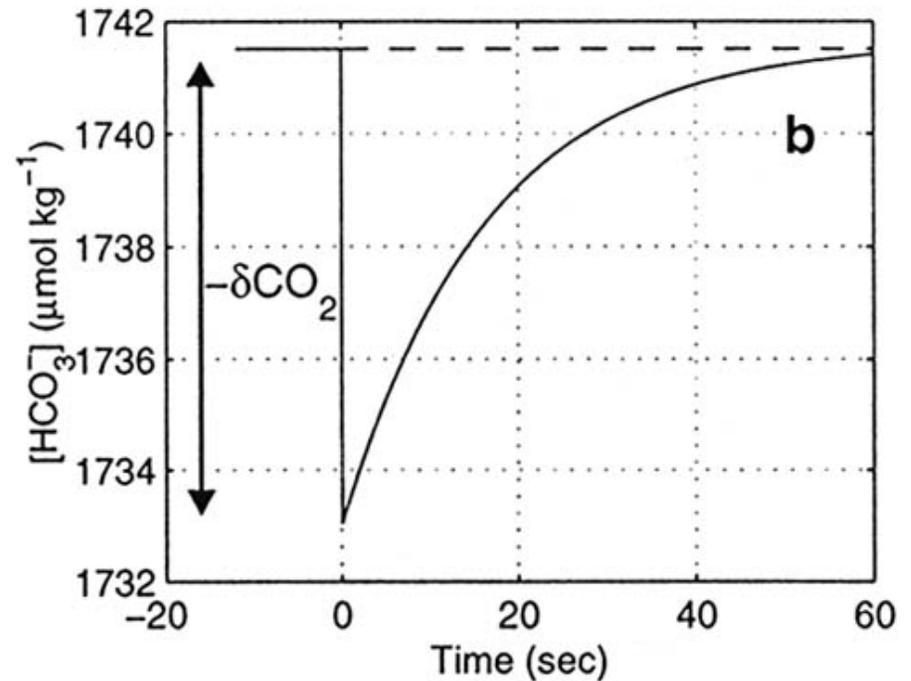
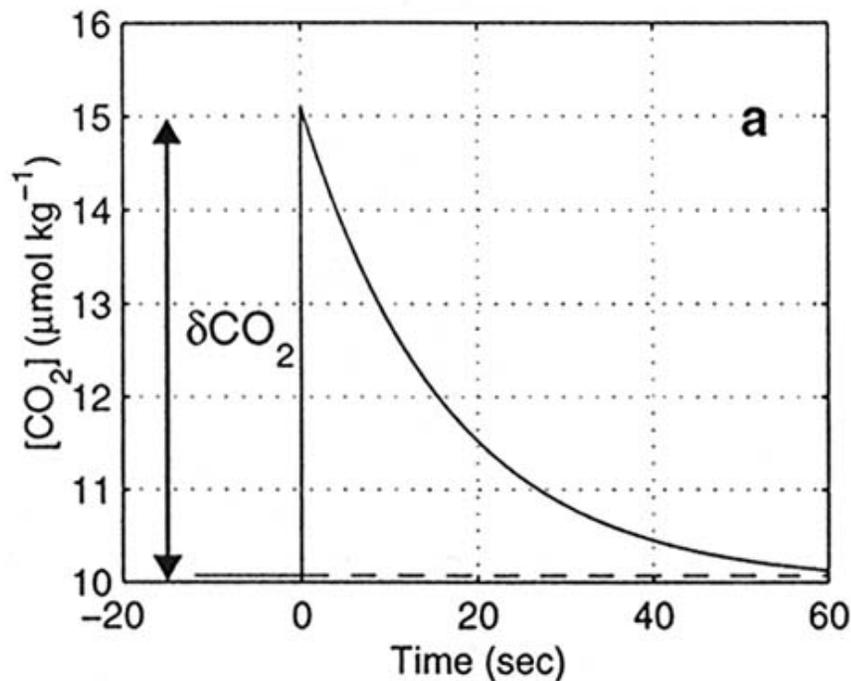
If we are to understand the science of a lower pH ocean we have to carry out predictive experiments. A concept sketch is shown here with supply of either acid or CO₂ to a set of experimental sites in much the same way that experiments are carried out on land. **There are fundamental challenges in this.**

Beyond Climate Cabled Experiment Concept



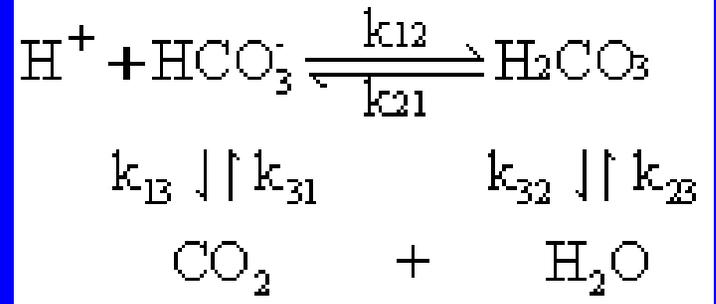
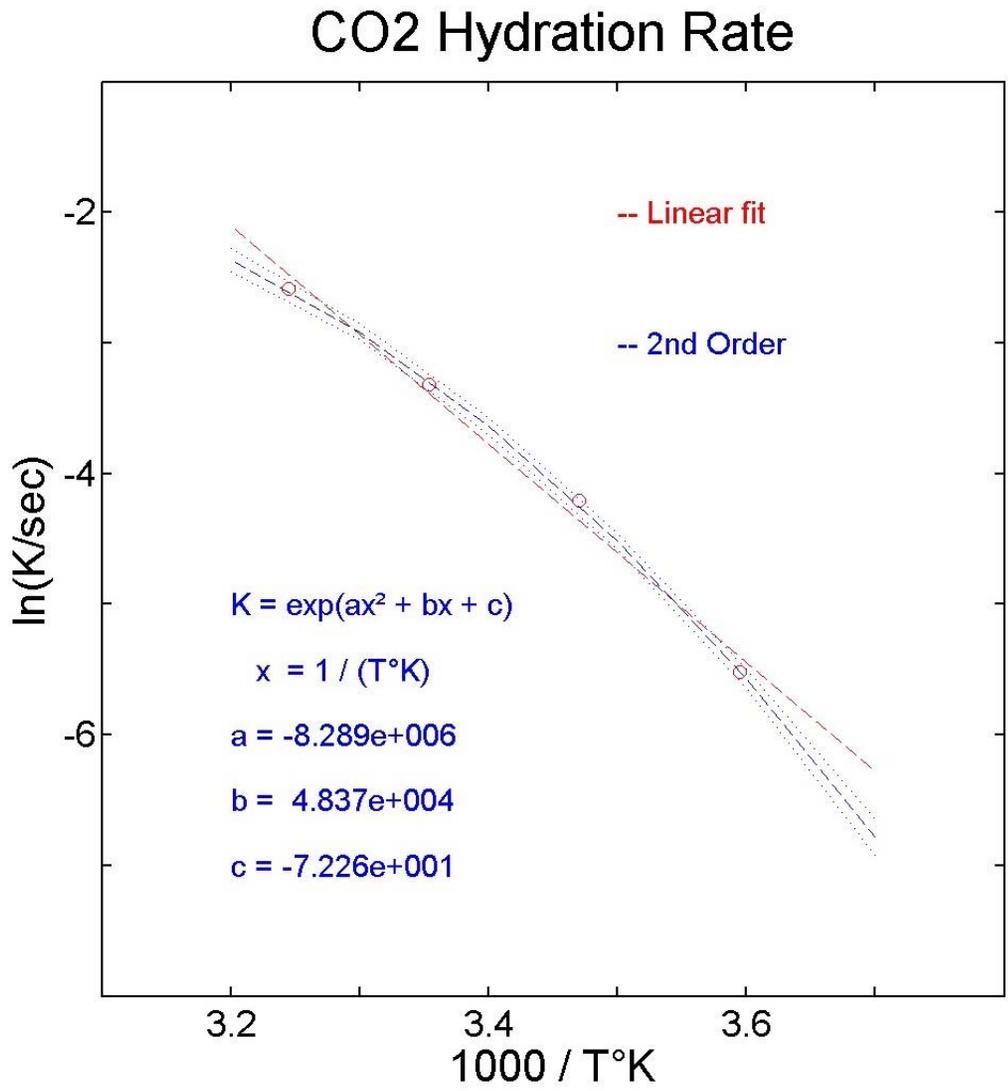
From Zeebe et al. (1998)

Time required (25°C, 1 atm.) for equilibrium in the ocean CO₂ 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 corals where pH underestimates the concentration of CO₂.



For CO₂ disposal we must use CO₂ itself. To simulate the emerging low pH ocean we may use acid addition to lower pH; there are kinetic challenges.

The CO₂ hydration rate constant (Johnson, 1982)



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 CO₂ produces a strong -Δ V, and thus the effect of pressure is to shift the equm. to the hydrated state – but the rates at pressure are unknown.

Analysis in terms of transition state theory

Human Carbonic Anhydrase – an ultra-fast zinc metalloenzyme for $\text{HCO}_3^- \leftrightarrow \text{CO}_2$

The essential function of an enzyme is to stabilize the transition state. The form of the $\text{CO}_2\text{-H}_2\text{O}$ 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 $\text{OH}^- + \text{CO}_2 \rightarrow \text{HCO}_3^-$. From Jonsson et al. 1978.

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

There is no potential energy barrier for 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 $\text{CO}_2 + \text{H}_2\text{O}$ reaction path.

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

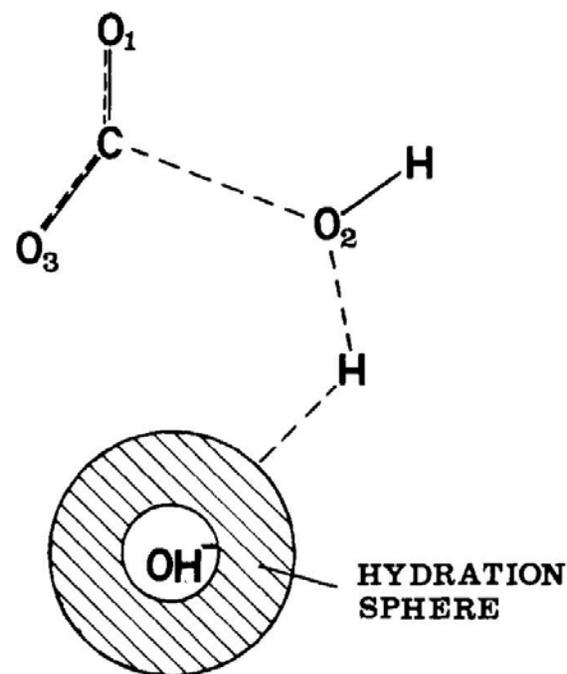


Figure 4. A possible transition state for the $\text{OH}^- + \text{CO}_2 \rightarrow \text{HCO}_3^-$ reaction in aqueous solution.

The Effect of Pressure on the Chemical Properties of Sea Water

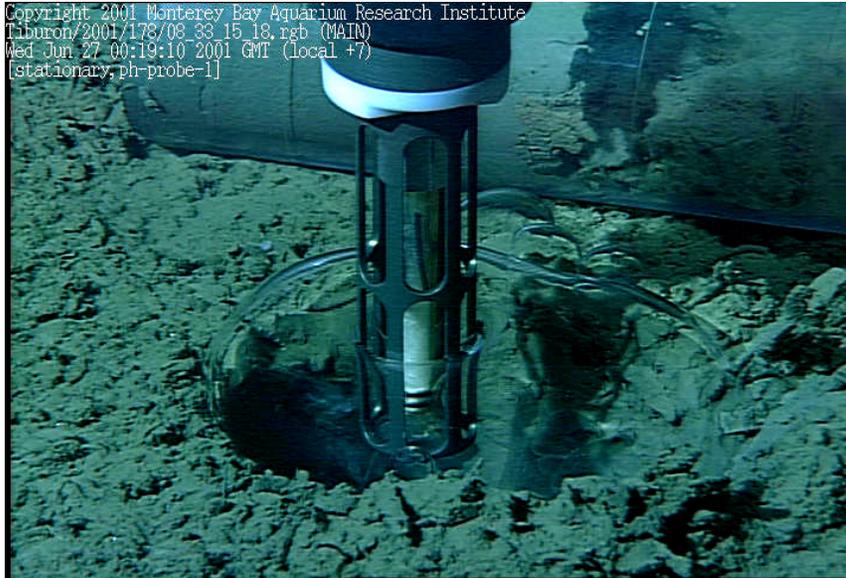
We can readily calculate the effect of pressure on the equilibrium state through knowledge of the equilibrium constants and the partial molal volume change for the reaction:

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

For the reaction of CO₂ with sea water we have a large ΔV of $-31 \text{ cm}^3/\text{mol}$, and thus we expect pressure to shift the system towards the lower volume state and favor the reaction.

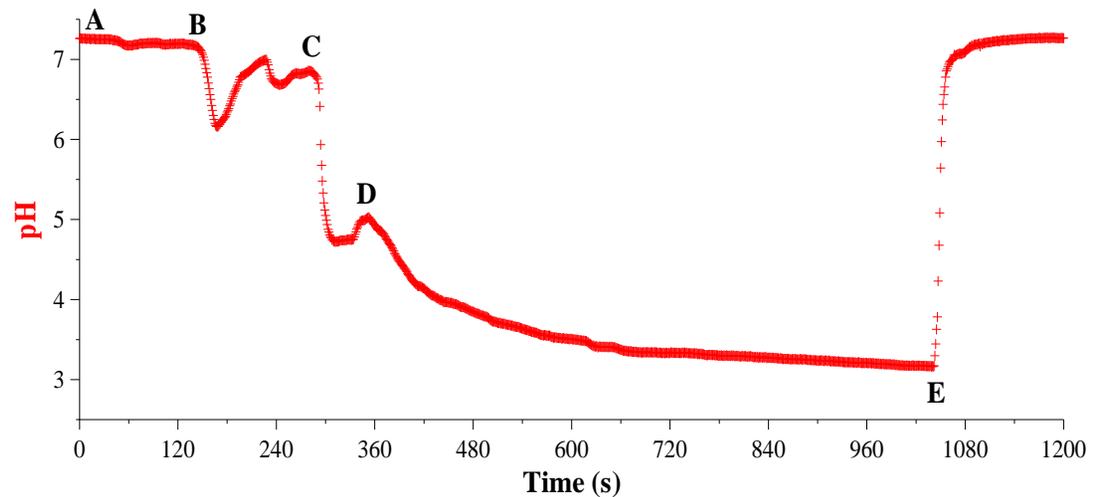
But we cannot predict the effect of pressure on the reaction rate – that must be determined experimentally.

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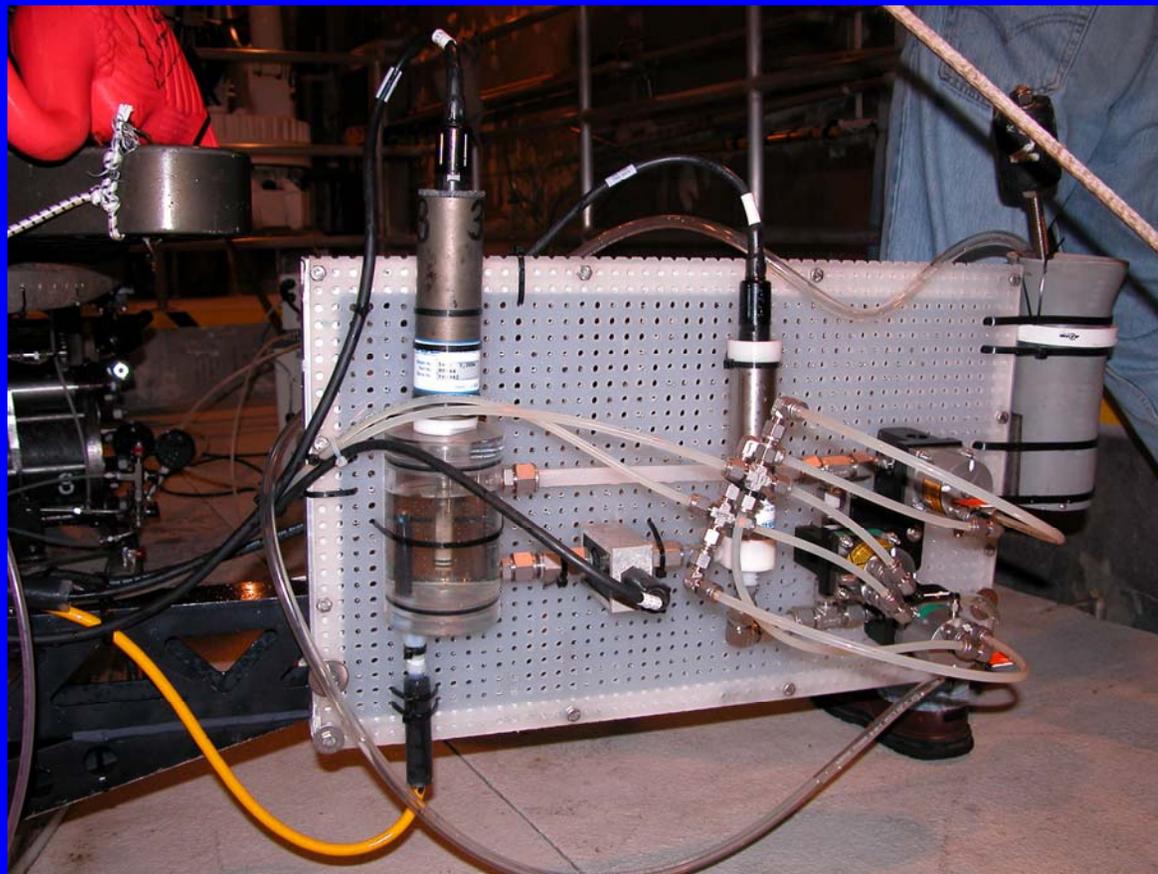


*An example of a sea floor CO₂ expt.
A pH electrode has been inserted into a
blob of CO₂ at 3600m depth. The
surface has deformed to form a water
pocket maintained by the strength of
the hydrate film.*

*We can follow the drop in pH as
CO₂ diffuses through the walls, and
forms a pool of dense low pH water.
The dissolution rate of CO₂ can be
estimated IF the system is at
equilibrium.*

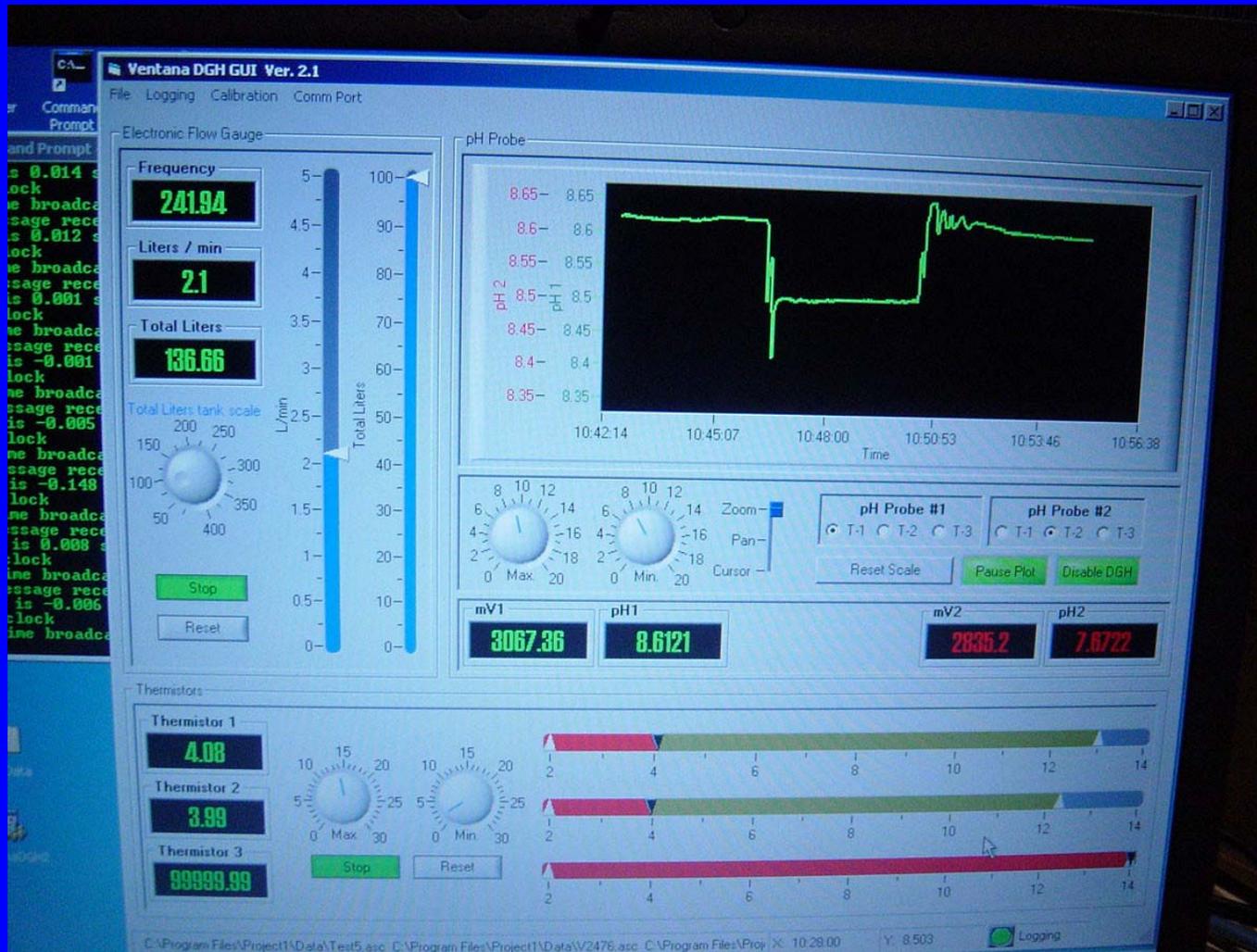


OACE 2 – pH equilibration cell for flow through, and looped circulation, to observe the time for CO₂ enriched water to reach pH equilibrium at 3940m depth, 1.6°C.



Observation: Once CO₂ enriched water was drawn into the cell we observed a drop in pH, indicating local dis-equilibrium. But the time to reach a stable signal was short – a few seconds. This indicates a strong pressure effect on the CO₂-H₂O reaction kinetics.

The slow hydration kinetics of CO₂ at low temperatures may not limit deep-sea CO₂ enrichment experiments. 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.)

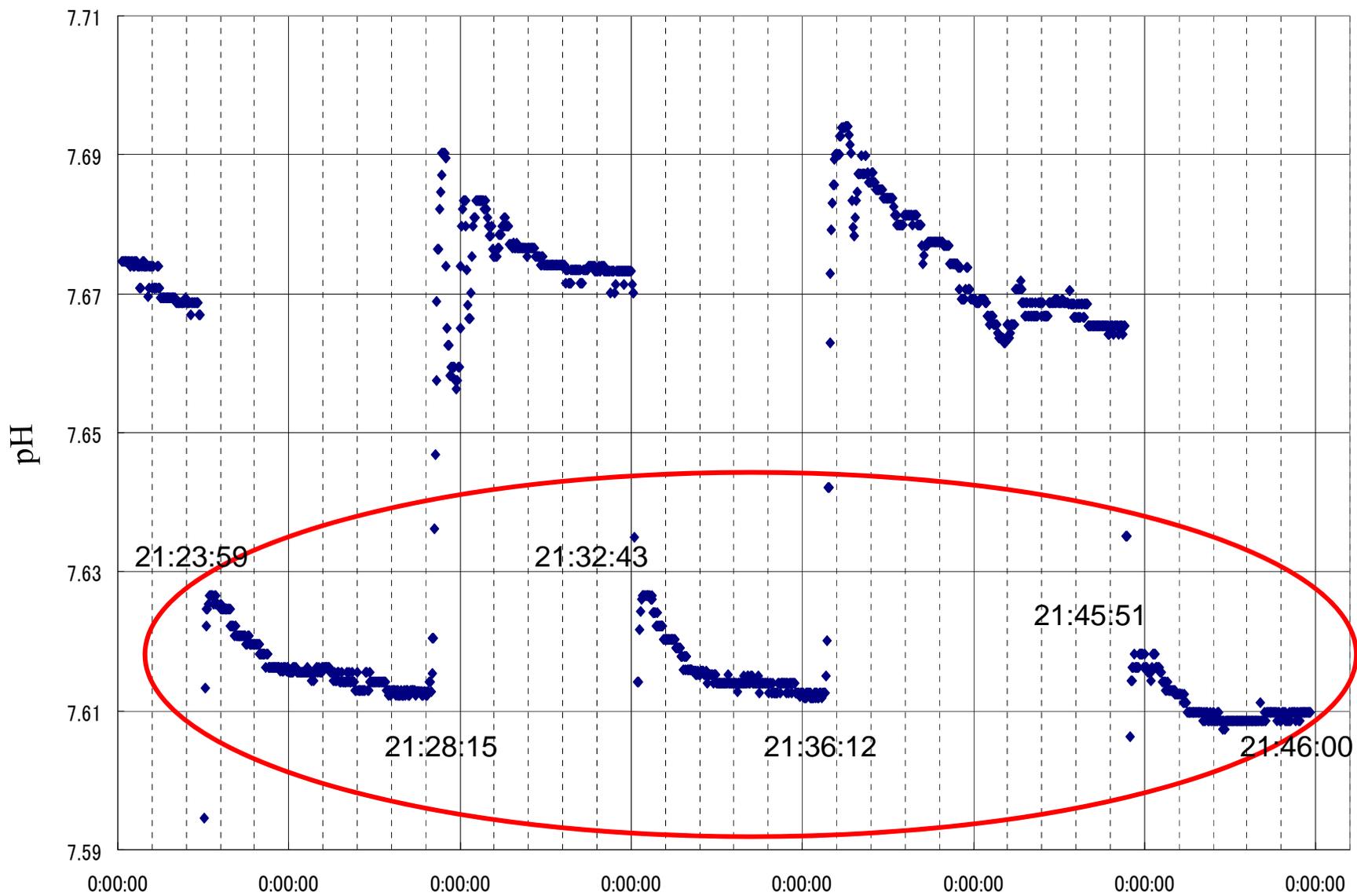


The increase in rate is extraordinary!!

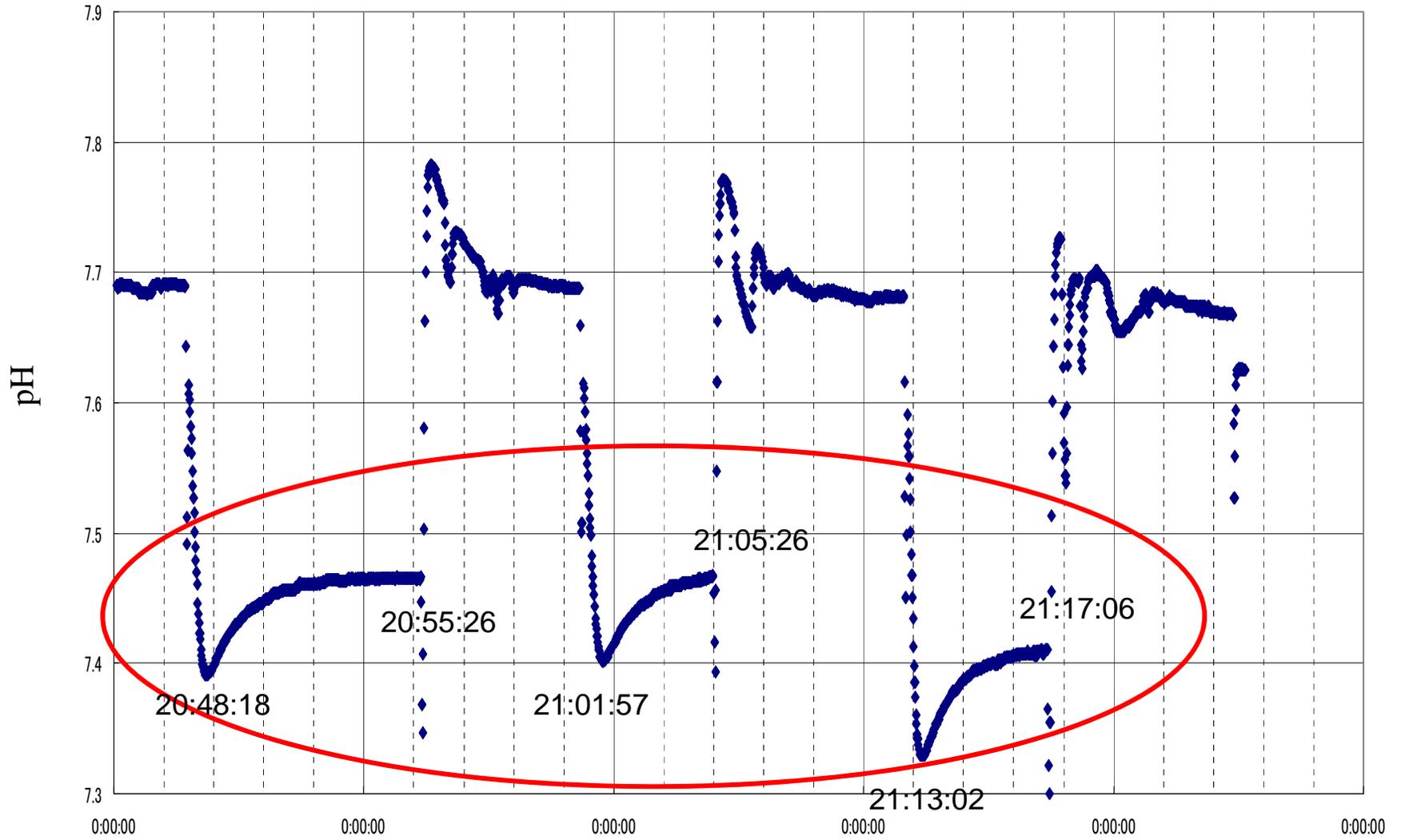
At 1 atmosphere this reaction would take ~ 20 minutes to complete.

Caution:
These data are new, and there may be artifacts of technique. But the basic approach is very testable. Role of Zn⁺ ?

D2476 500m Add 1-stroke acid of HCl



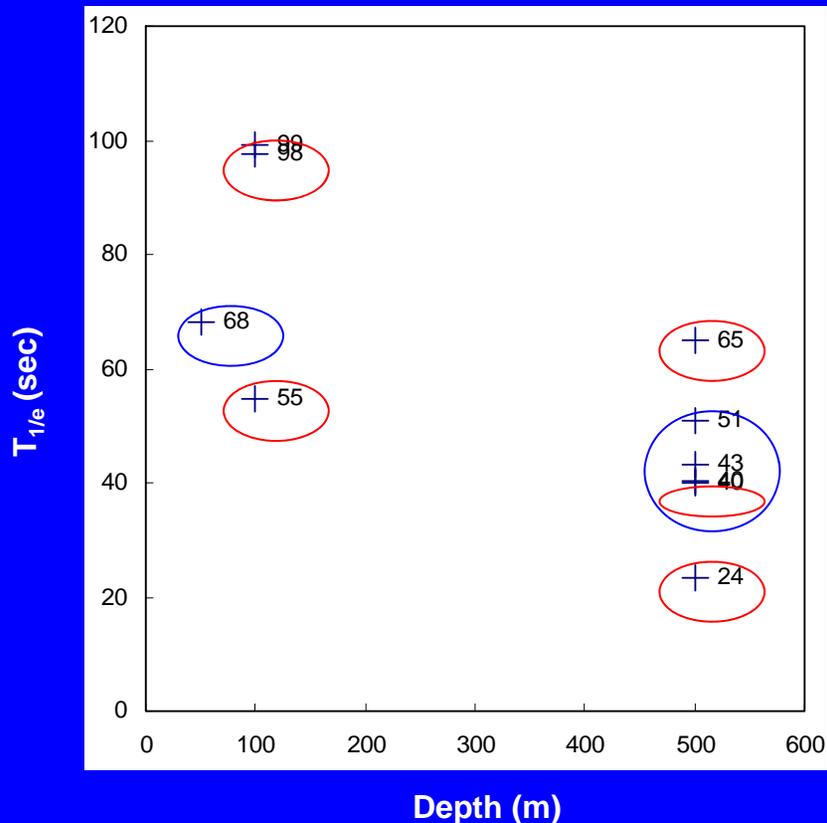
D2476 500m CO2 delivery



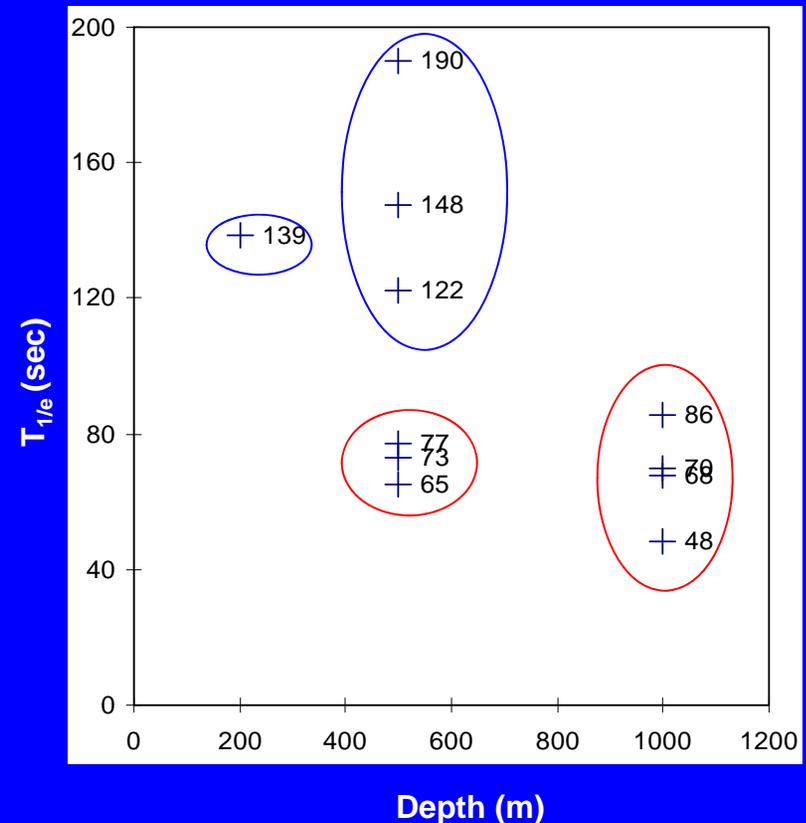
Preliminary analysis of the e-folding time for acid and CO₂ perturbation experiments in situ. The time scale for CO₂ is ~ 2x that for H⁺.

From Nakayama et al. In Prep.

Add HCl In situ



CO₂ delivery In situ



While these data do not substitute for a formal analysis of the effect of pressure on the rate constants (TBD), they serve as a very practical test of the relaxation time of a complex solution at low temperature and high pressure.

○ D 2475
○ D 2476

Ab Initio Molecular Orbital Calculations on the Water-Carbon Dioxide System. The Reaction $\text{OH}^- + \text{CO}_2 \rightarrow \text{HCO}_3^-$. From Jonsson et al. 1978.

The transition state identified in the gas phase is also valid for the $\text{CO}_2 + \text{H}_2\text{O}$ reaction path.

There is no potential energy barrier 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.

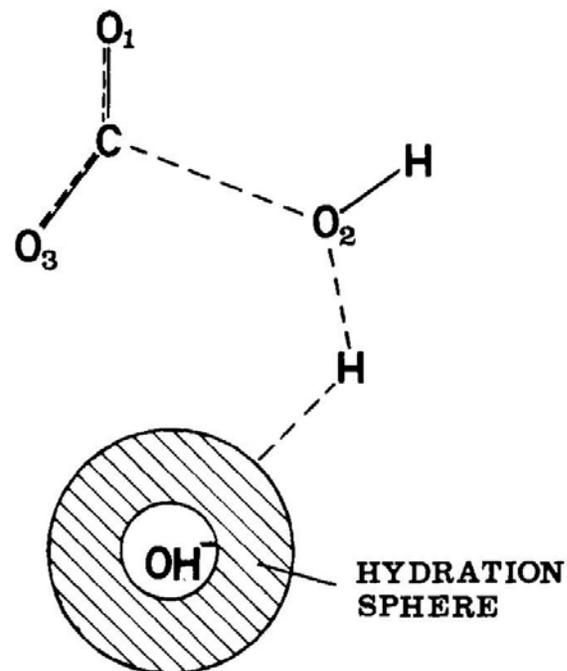


Figure 4. A possible transition state for the $\text{OH}^- + \text{CO}_2 \rightarrow \text{HCO}_3^-$ reaction in aqueous solution.

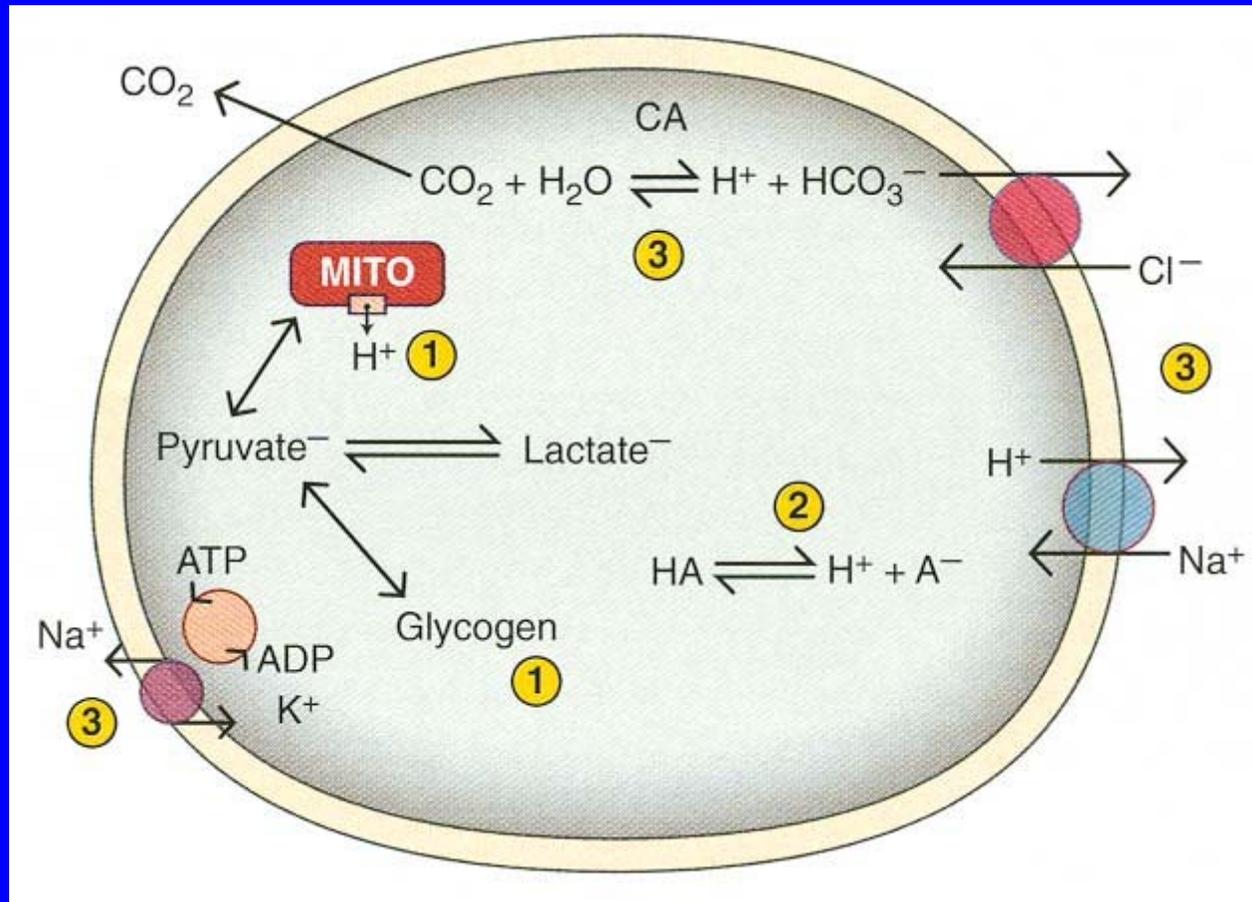
One effect of pressure may be to change the hydration sphere of the dangling proton thus greatly increasing the reaction rate

***Sunset over an ocean now > 0.1 pH units lower than pre-industrial.
About 50% of the 400 billion tons of fossil fuel CO₂ now stored in the
ocean is in the upper 250m.***



From Seibel and Walsh (2001):

Regulation of intracellular pH in an animal cell.



1. Inter-conversion of acids and bases.
2. Buffering: HA is a weak acid.
3. Transport of acids/bases across cell membrane. Carbonic anhydrase (CA) catalyses dehydration and hydration of CO_2 .

MITO = mitochondrion