Experimental Design for Ocean Acidification Impact Studies

21st Pacific Science Congress, Okinawa, 2007

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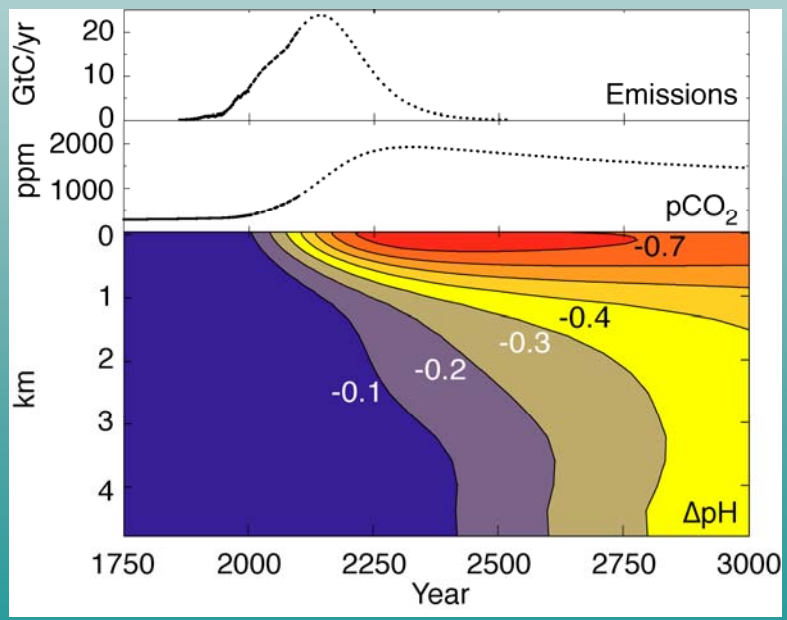


The world is grappling with Greenhouse Gas policy issues

- *In the classic human sequence : Denial, Anger, Bargaining, Acceptance the world is now at the bargaining stage for an energy/CO2 policy*

- *But what stage will we bargain to? – And who speaks for the oceans?*

- *Most competent and informed specialists do not believe that stabilization of atmospheric CO2 levels at 550 ppmv is possible. There is some optimism that 650 ppmv will be achievable, but not without vast changes in the global economy. Slowed growth is more likely.*

- *This implies ocean pH changes > 0.3 within the lifetime of a graduate student today; and very likely >0.5 in the future.*

- *We do not understand the consequences of this for ocean ecosystems, and it has not been seen on earth for millions of years*

- ***We lack many basic verifiable experimental techniques and data to support claims of benign or malign consequences***

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

pH

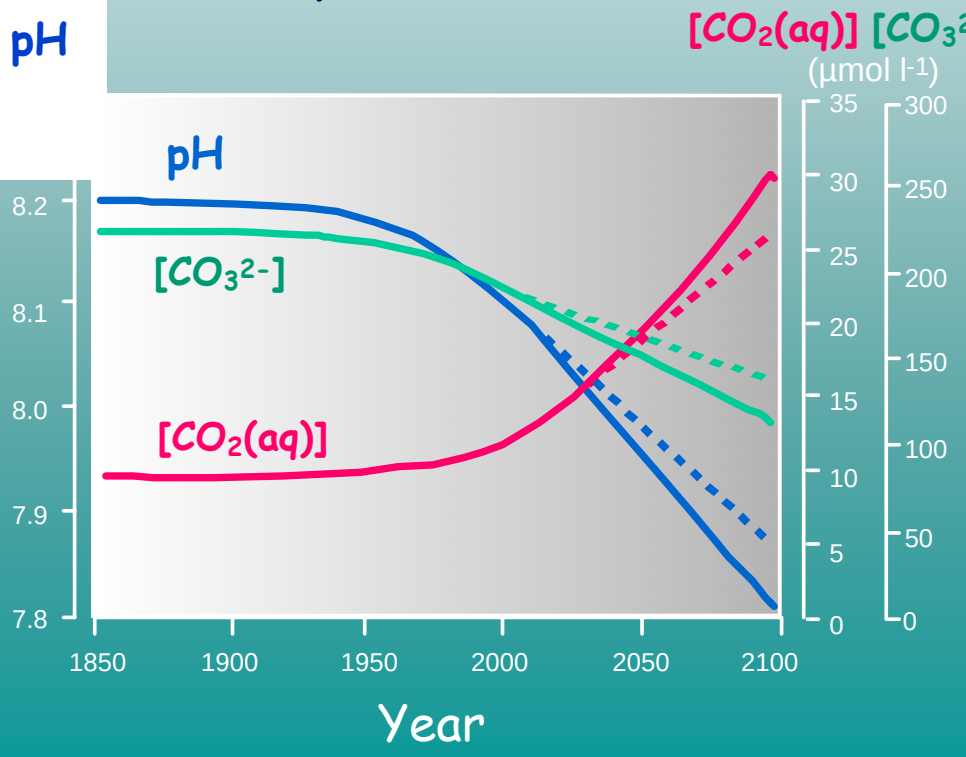
From Brewer 1997

The log scale for pH often confuses the lay person. The drop in carbonate ion, and indicator of ease of formation of carbonate skeletons, will be dramatic

An Inconvenient Truth part 2:

There is very little doubt that the CO2 trend will continue to rise – the time scale is really the only thing in question. We will transfer several trillion tons of CO2 to the ocean even under the most optimistic scenarios

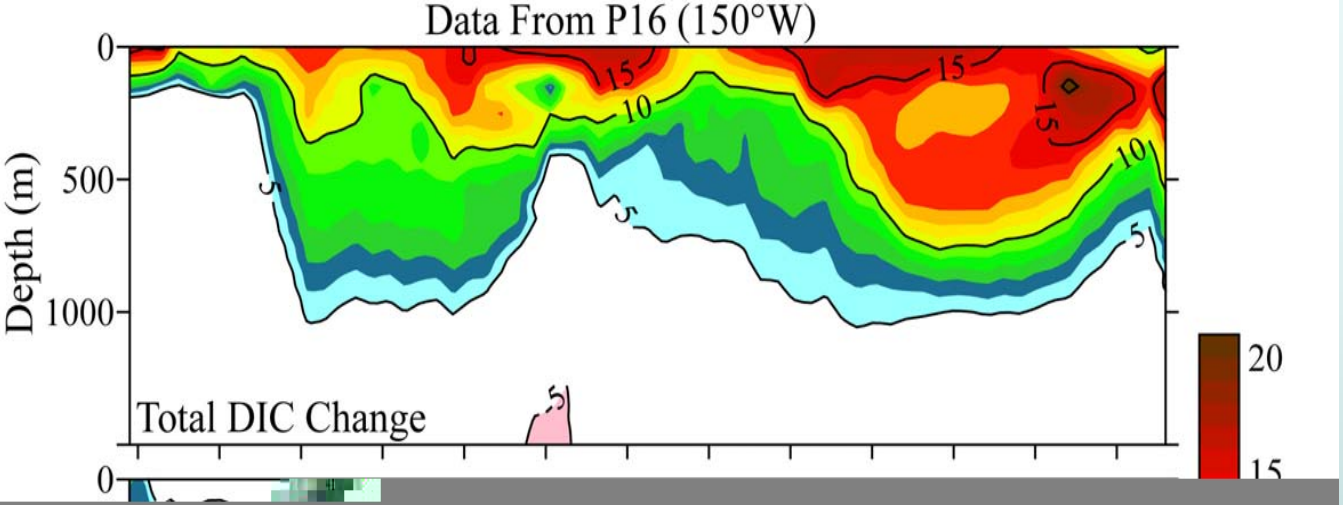
Surface Ocean



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



Total DIC change over 15 years in the Pacific

DIC change due to ventilation and respiration processes

DIC change due to uptake of anthropogenic CO_2

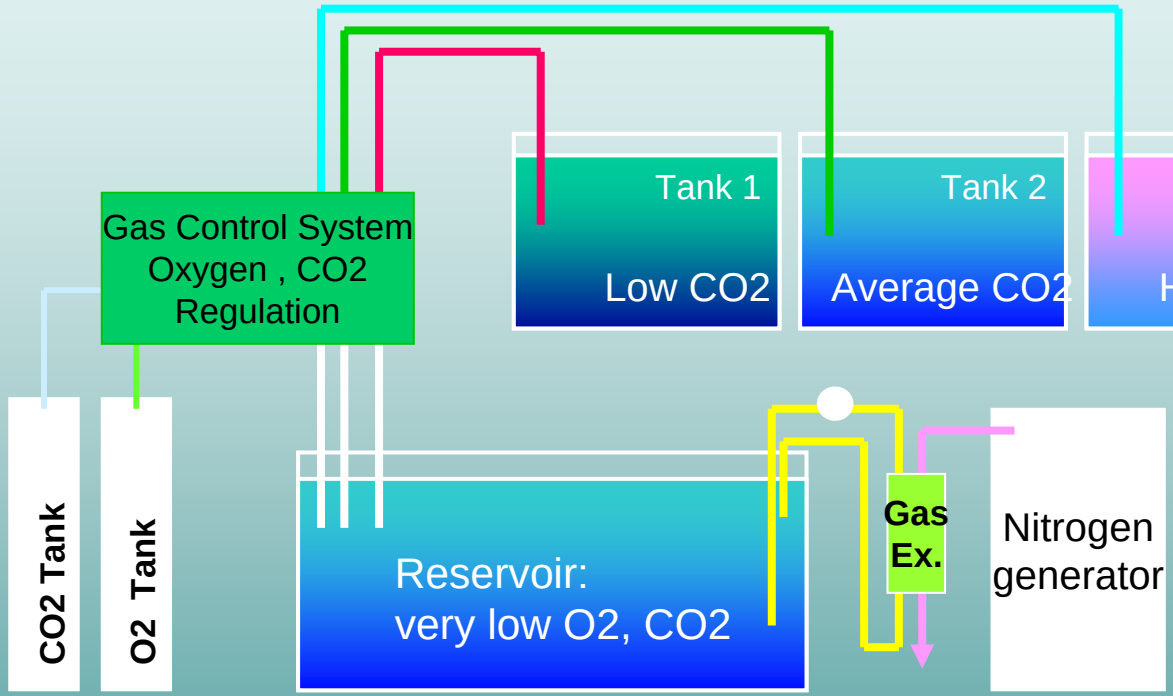
Sabine et al. (in prep)

Elevated CO_2 Effects on calcification in phytoplankton

With Ulf Riebesell on the mesocosm raft at the Espegrend field station, Bergen, on a gray day.

On the raft examining the 10m deep bags controlled to glacial, pre-industrial, modern, and 2100 pCO_2 levels.

Controlled-gas Aquarium System for lab-based studies of CO2 tolerance – *Barry Laboratory*



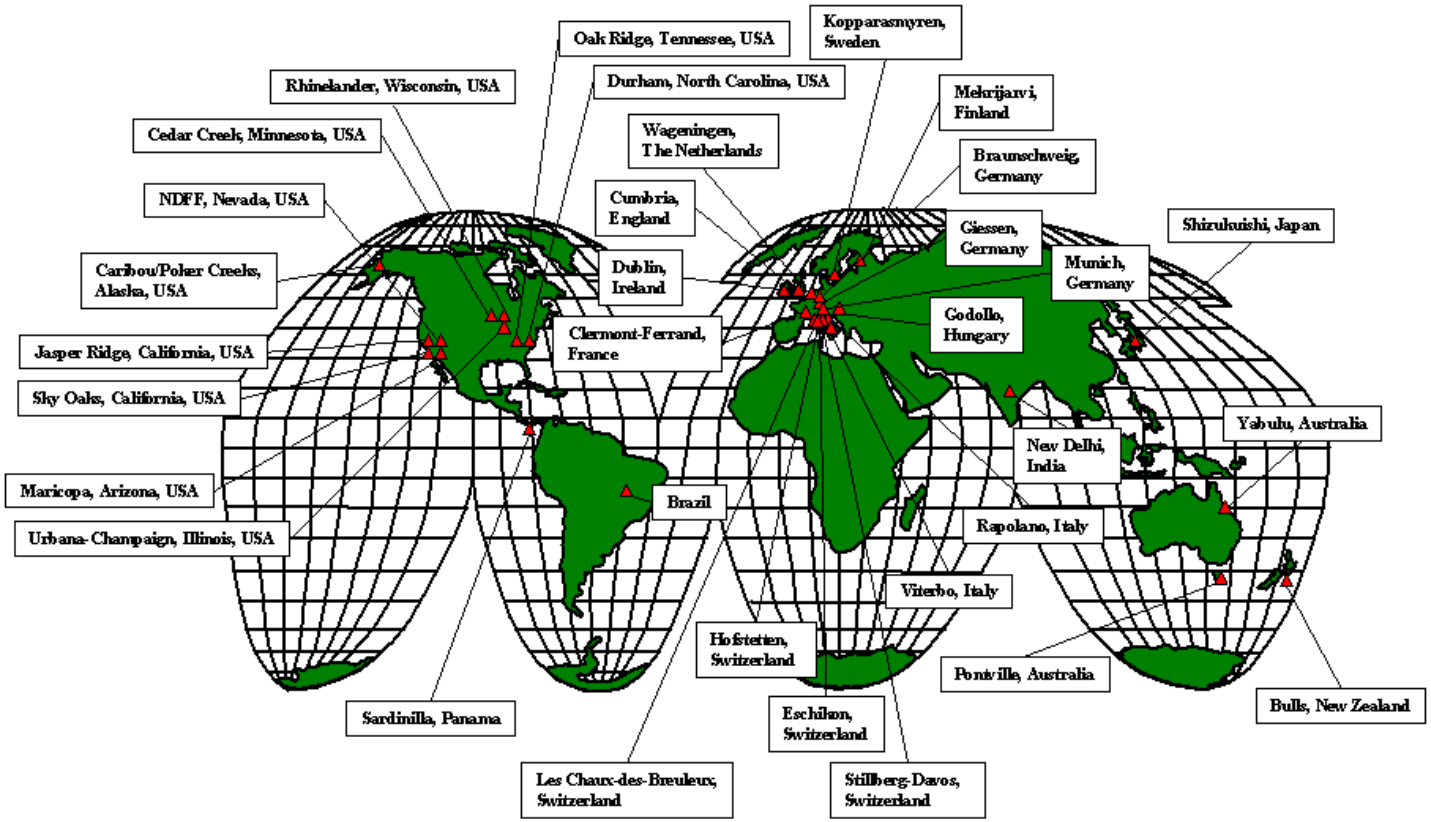
- Control of temperature, oxygen, carbon dioxide
- Use:
  - Studies of chronic hypercapnia on marine animals
  - Growth rates, respiration, physiology

How might we design more open in situ controlled ocean CO_2 perturbation experiments that have useful predictive value?

We first looked on land at the very large scale experiments there. The permitting issues are few, the time scales long, and infrastructure is easy.

Very large quantities of CO_2 are required to carry out these studies.

FACE Experimental Sites *– Why are there no ocean CO_2 sites?*



Will we get it right? – A matter of skill

Plant Productivity Benefits of High Carbon Dioxide Busted

Although rising CO_2 levels may reduce global crop yields through the effects of higher temperatures and decreased soil moisture, arguments have been made that direct fertilization effects will more than offset these losses. **Long *et al.*** (p. 1918; see the Perspective by **Schimel**) present a critical analysis of data on which the Intergovernmental Panel for Climate Change base their projections that elevated

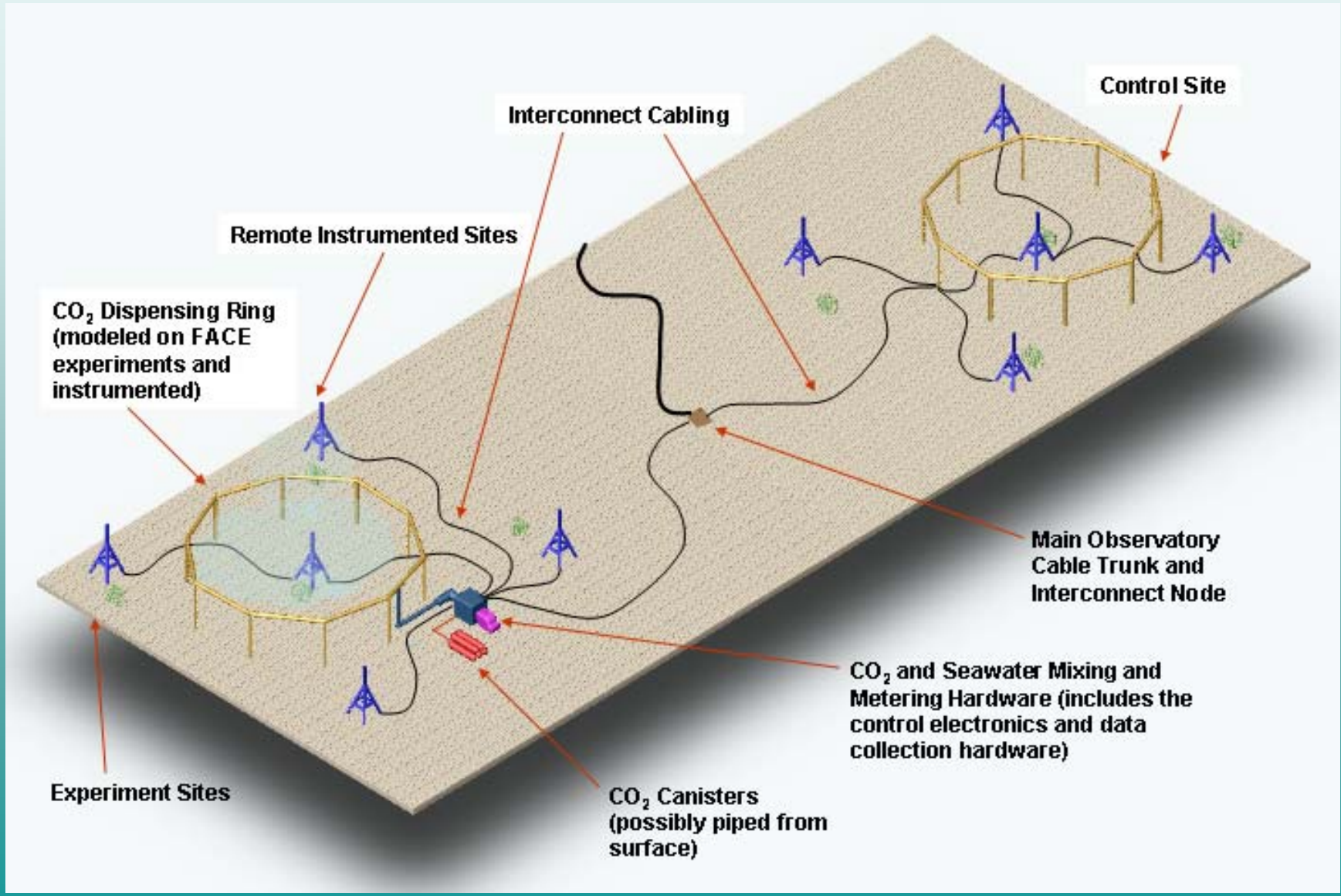
Recent work shows that claims of land plant fertilization from higher CO2 levels have been overstated by ~50%. The early work on enclosures is undone by truly open experiments. How well can we predict oceanic effects with today's techniques?

Food for Thought: Lower-Than-Expected Crop Yield Stimulation with Rising CO_2 Concentrations

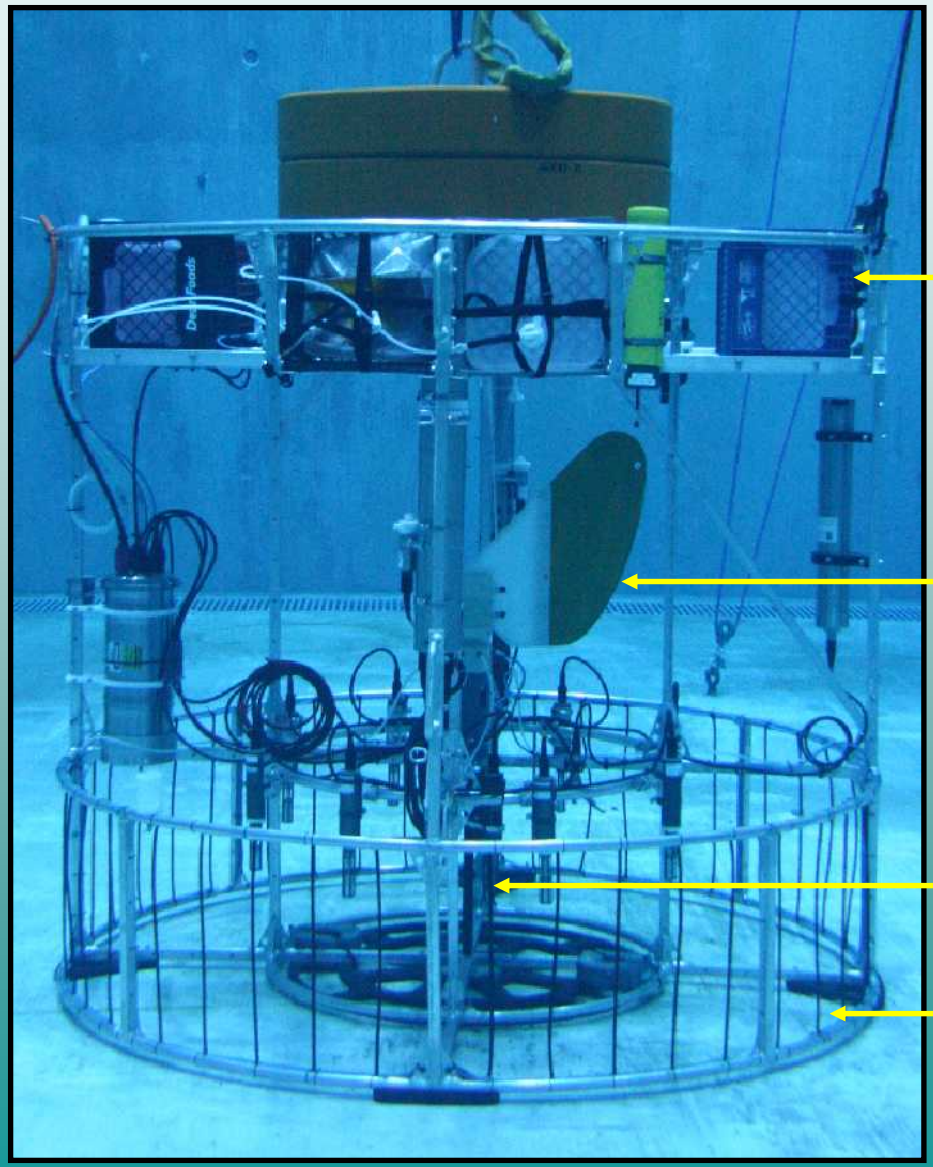
Stephen P. Long,[1,2,3]* Elizabeth A. Ainsworth,[4,1,3] Andrew D. B. Leakey,[3,1] Josef Nösberger,[5] Donald R. Ort[4,1,2,3]

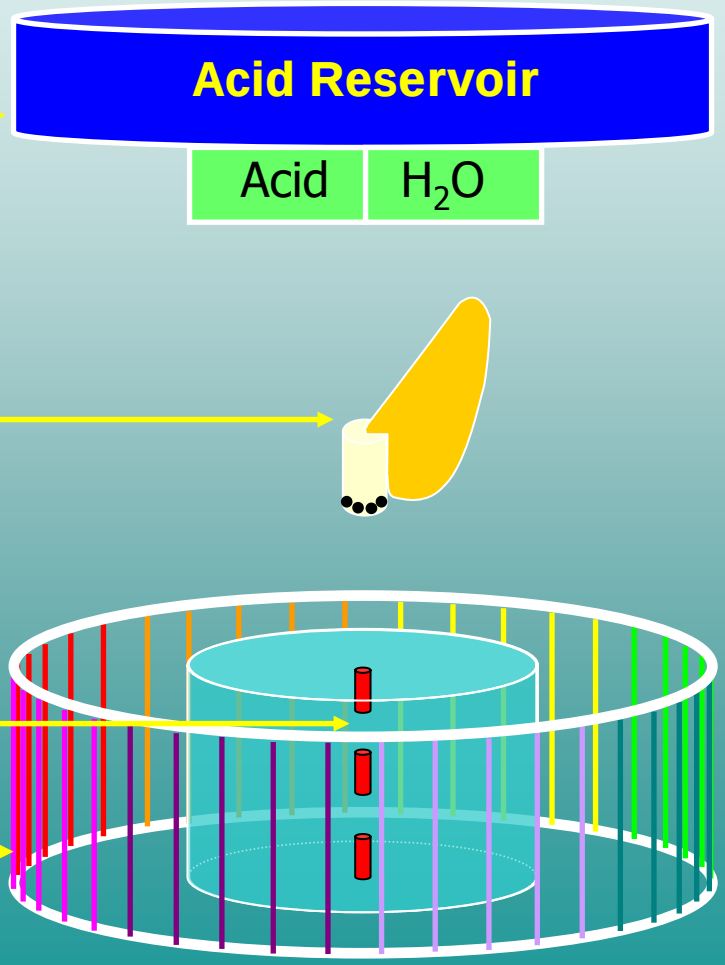
Model projections suggest that although increased temperature and decreased soil moisture will act to reduce global crop yields by 2050, the direct fertilization effect of rising carbon dioxide concentration ($[CO_2]$) will offset these losses. The CO_2 fertilization factors used in models to project future yields were derived from enclosure studies conducted approximately 20 years ago. Free-air concentration enrichment (FACE) technology has now facilitated large-scale trials of the major grain crops at elevated $[CO_2]$ under fully open-air field conditions. In those trials, elevated $[CO_2]$ enhanced yield by ~50% less than in enclosure studies. This casts serious doubt on projections that rising $[CO_2]$ will fully offset losses due to climate change.

Original concept sketch for FOCE – the ocean equivalent of land experiments

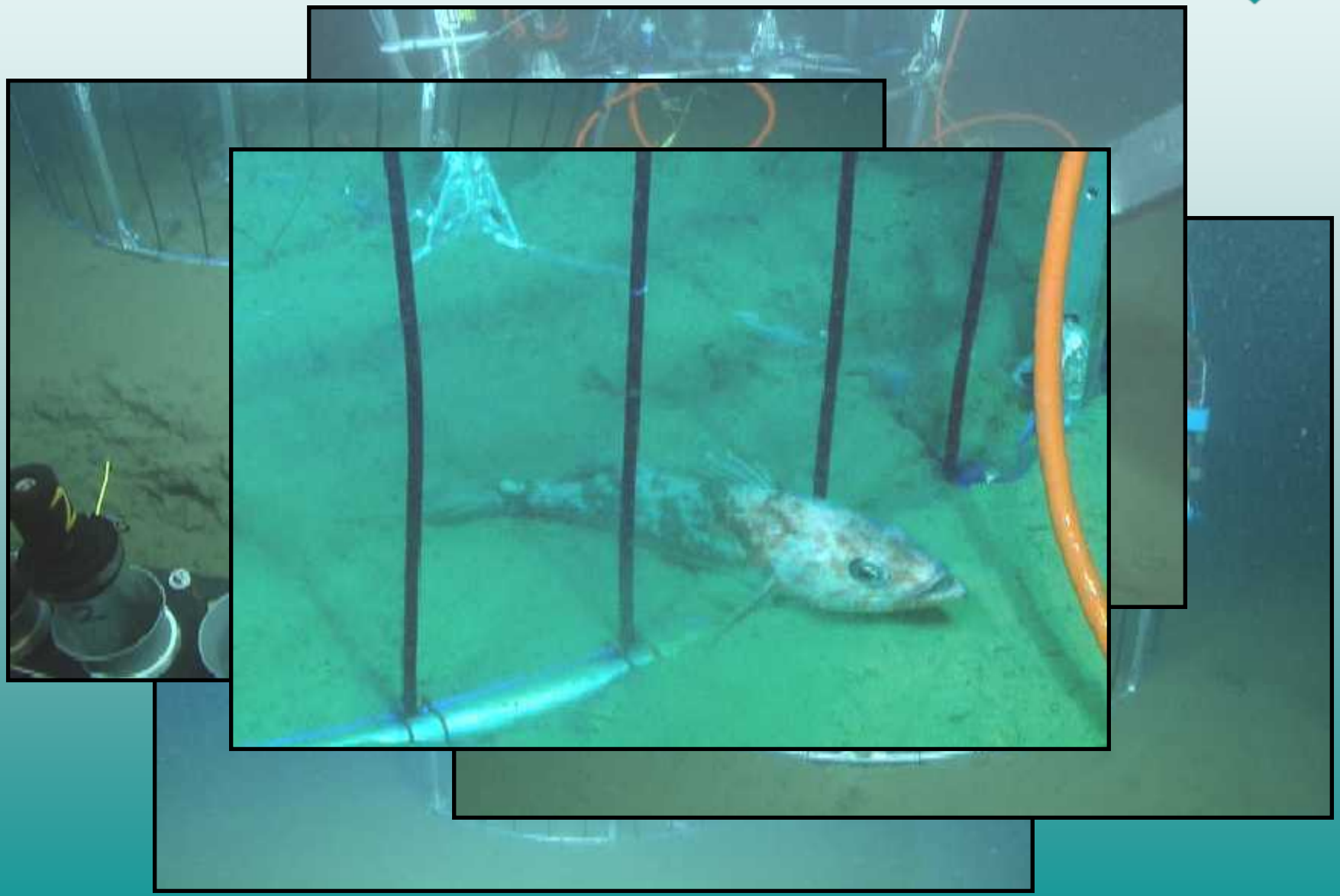


The FOCE Prototype – a double ring with acid emitters and sophisticated valve control to allow for system latency

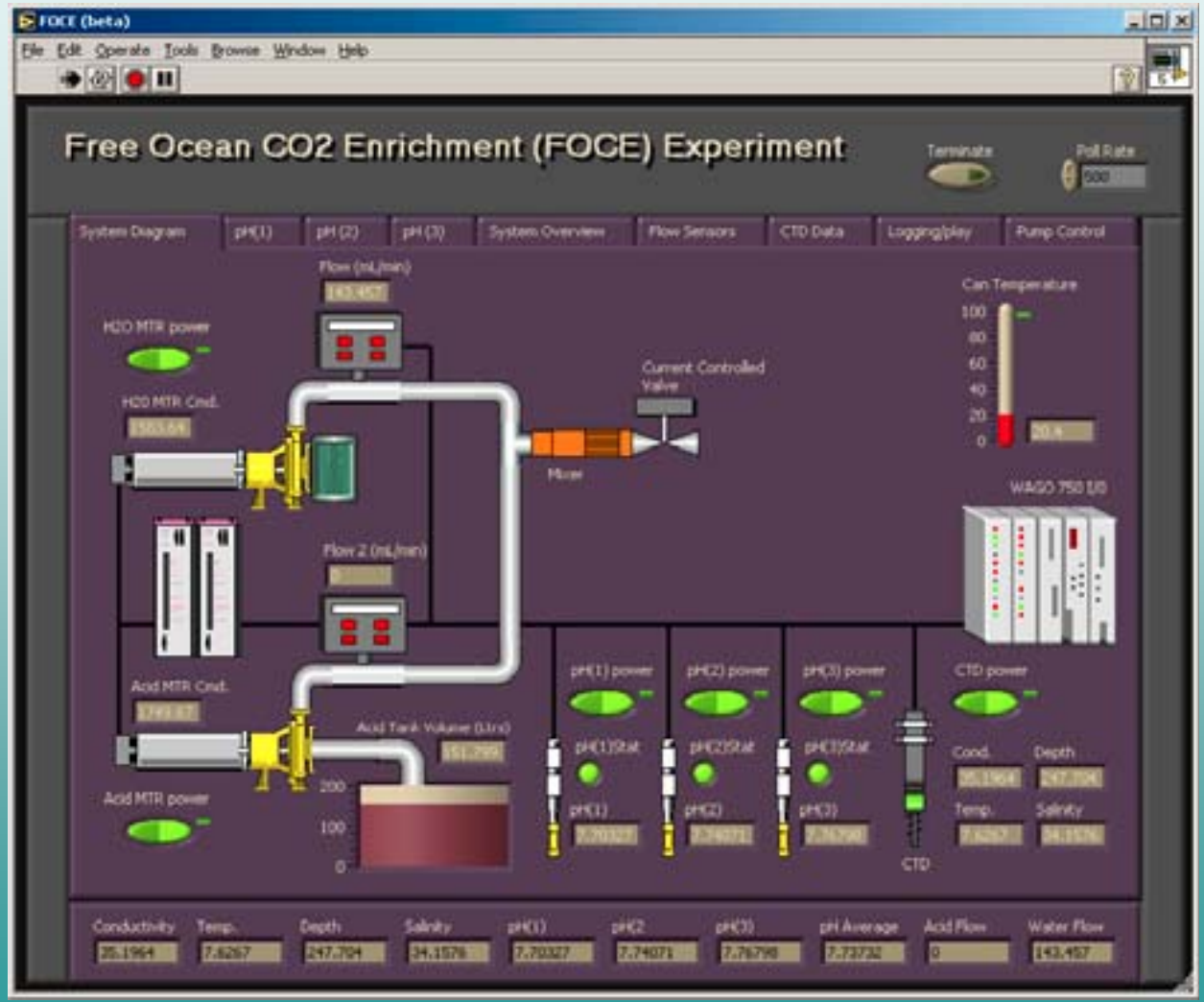




Field Trial: On the Seafloor



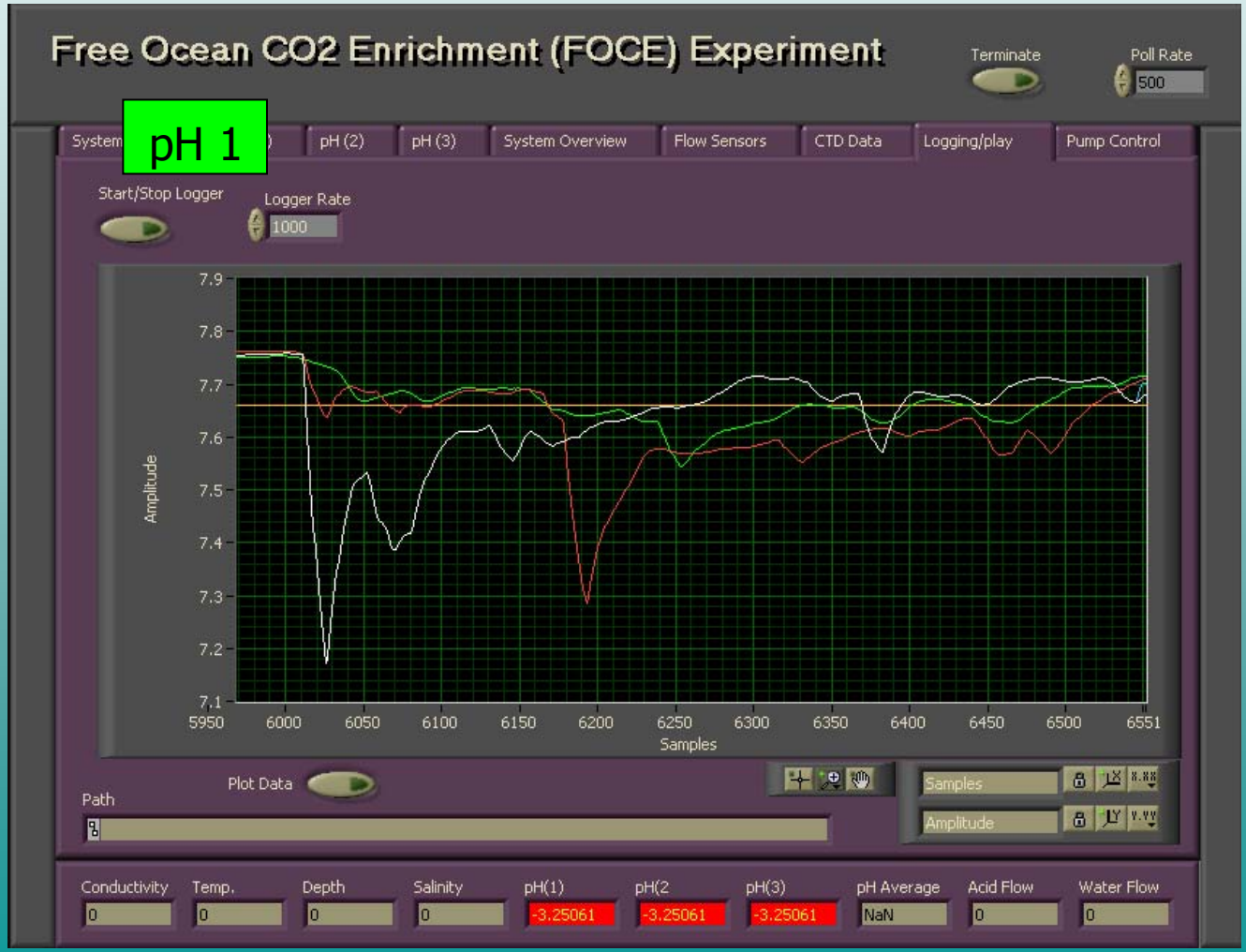
Prototype FOCE GUI for control



The GUI allowed operator control over various set points to initialize the acid injection, and water-acid mixing rates, and to select of de-select electrodes for the control loop. Once the basic system was initialized then automatic control took over, with maintaining the ΔpH band being the control target

Field Trial: Data & pH Control

We were successful in constructing a complex delivery and control system with feedback accounting for latency – but the Δ pH was less than desired



There are two basic problems which are inter-related:

The water residence time is short, and the reaction kinetics are slow.

Can this problem be solved?

In air only mixing is required – in sea water we deal with complex reactions with finite (slow) rates

Some technical detailed knowledge is required to control the system

- The equations below are taken from the model of Zeebe and Wolf-Gladrow

$$CO_2 + H_2O \underset{k_{-1}}{\overset{k_{+1}}{\rightleftharpoons}} HCO_3^- + H^+$$

$$CO_2 + OH^- \underset{k_{-4}}{\overset{k_{+4}}{\rightleftharpoons}} HCO_3^-$$

$$CO_3^{2-} + H^+ \rightleftharpoons HCO_3^-; \qquad K_2^* = \left[CO_3^{2-}\right]\left[H^+\right] / \left[HCO_3^-\right]$$

$$H_2O \rightleftharpoons H^+ + OH^-; \qquad K_W^* = \left[H^+\right]\left[OH^-\right]$$

;

$$\frac{\mathrm{d}(\delta \mathrm{CO}_2)}{\mathrm{d}t} = -\frac{1}{r}\delta \mathrm{CO}_2$$

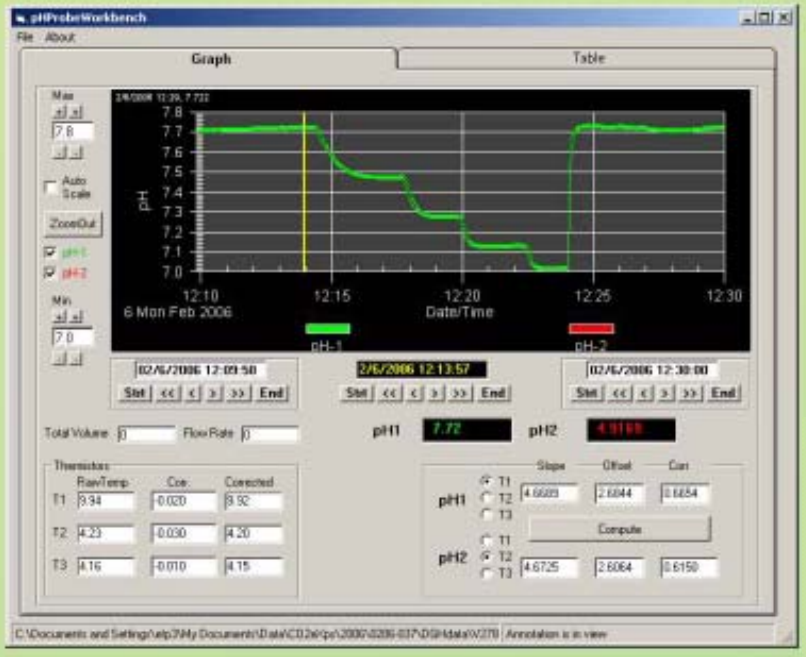
where the relaxation time is given by

$$\frac{1}{r} = +k_{+1} - k_{-1}\left(\partial_s b\left[H^+\right]^* + \partial_s h\left[HCO_3^-\right]^*\right)$$

$$-k_{-4}\partial_s b + k_{+4}\left(\left[OH^-\right]^* + \partial_s oh\left[CO_2\right]^*\right)$$

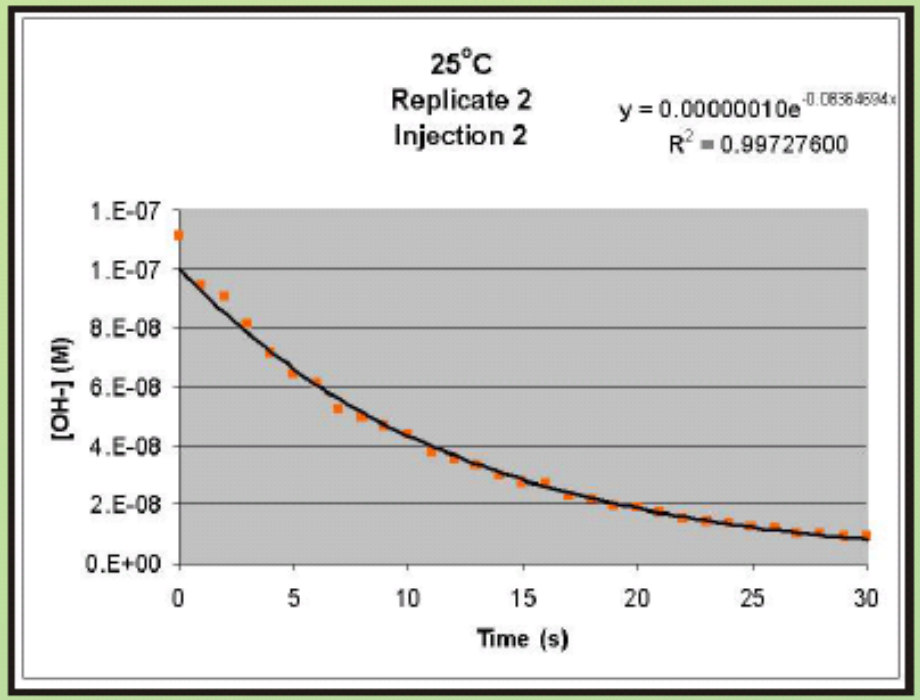
This model has never been experimentally verified – until now

We have carried out the first field test of the Zeebe & Wolf-Gladrow model as a critical part of Initiative planning

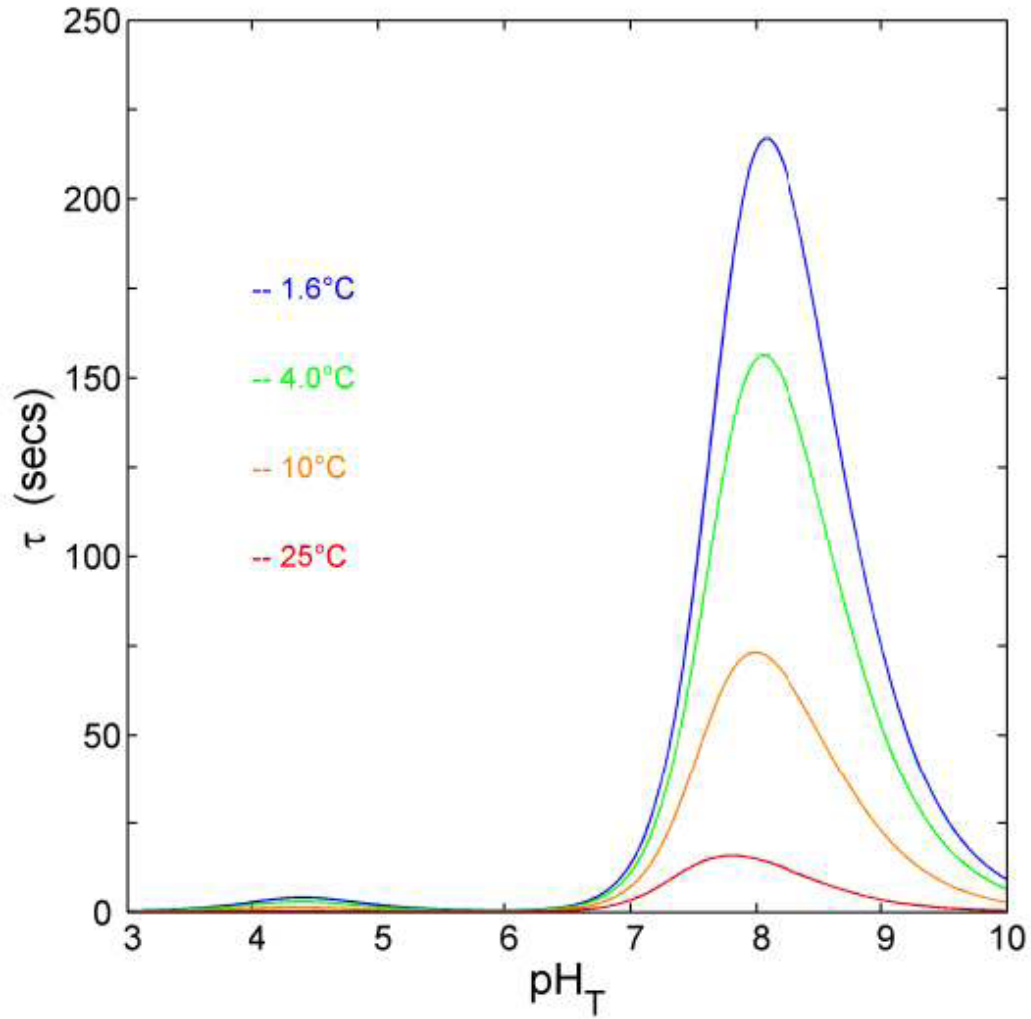


We enclose a volume of sea water, and inject precise amounts of acid or CO2, then follow the pH decay curve, in practice we compute and model OH -

The precision is ± 0.001 pH units; the curve observed is compared with theory. We find small errors at depth, likely due to the pressure terms.



Implementing the Zeebe- Wolf-Gladrow kinetic model – T and pH dependent



The model yields a highly non-linear curve with very strong pH dependency. The reaction is quasi-autocatalytic in that as pH drops the reaction goes faster. Normal sea water is near the peak and in a very steeply sloping region.

For warm surface water (coral reef) experiments a residence time in the perturbation area of about 2 minutes is required for significant equilibration. Cold, deep waters are lower pH and the residence times are longer.

How much CO_2 is required?

- For a typical surface sample (S= 35, T=22°C, TA = 2300, Initial pH = 8.1)

then to achieve a ΔpH of 0.5 we need ~236 μmol CO2.

- For a typical deep-water sample (S=34, T=4°C, TA=2400, Initial pH = 7.6)

then to achieve a ΔpH of 0.5 we need ~184 μmol TCO2.

Thus for a useful approximation:

We need to deliver ~200 μmol CO2 per kg to achieve a 0.5 pH reduction.

A corral of 2m diameter and 1m high contains 3,140 liters volume. Thus to perturb the pH of this system by 0.5 pH units we need 628 mmols CO_2. For a fully open system the pump requirements for flooding the experimental volume with enriched sea water are large. Our design study shows that the power/size needs can be easily met by the NSF Cabled Observatory system. But the permit requirements would be difficult, and many non-MBARI sites would find these requirements hard to meet. This leads to examination of partially open system designs.

Dealing with flow

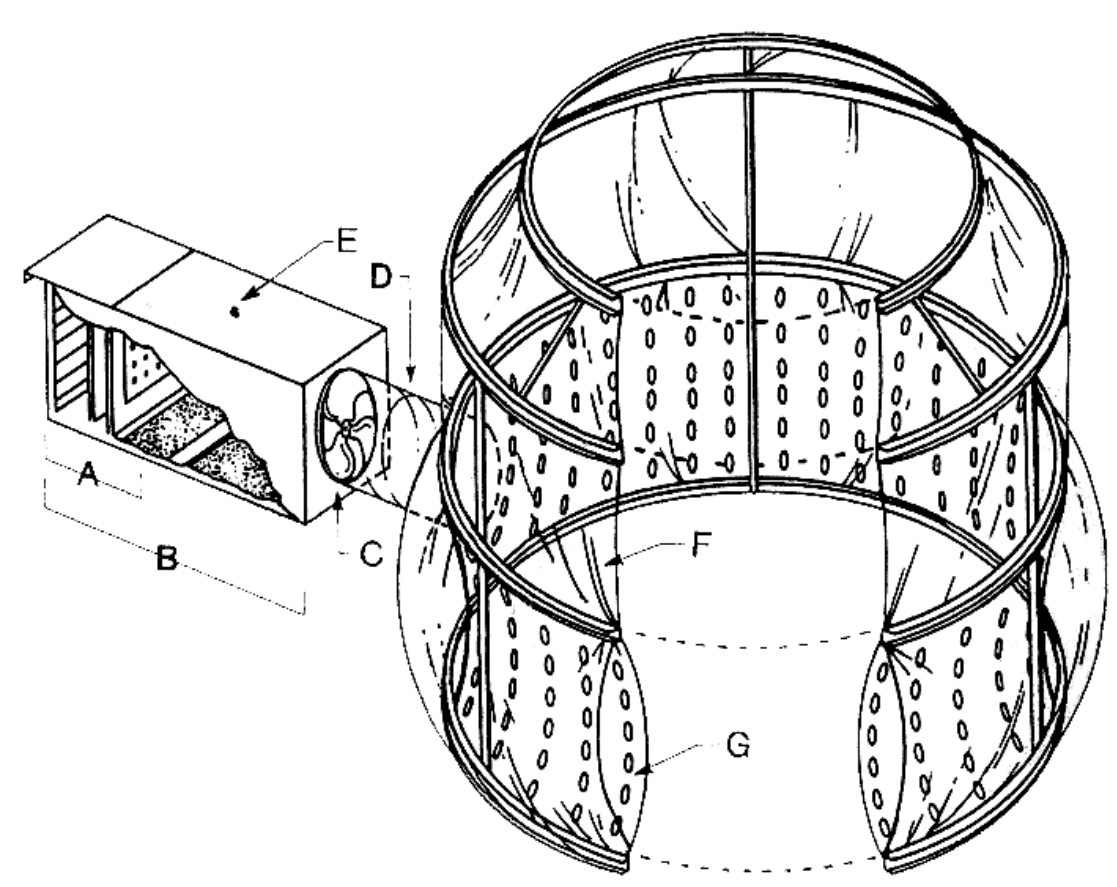
Dealing with flow

If the water velocity is 1 cm/sec then:

- The residence time within the 2m diameter corral is 3.33 minutes
- we need to supply CO_2 at a rate of 188 mmols/minute.

- We should design for higher flow rates, say up to 4 cm/sec, thus these numbers could be ~ 752 mmols/minute.
- For a group of 4 corrals this is about 200kg/day (about 73 metric tons per year for the 4cm/sec scenario). This is large by oceanic standards, but small for terrestrial (FACE) releases that have reached 1000 tons/year.
- Suggests examining smaller scale systems for the pilot program.

Relationship to early atmospheric enrichment studies - 20 years ago!



From: Direct Effects of Increasing CO_2 on Vegetation

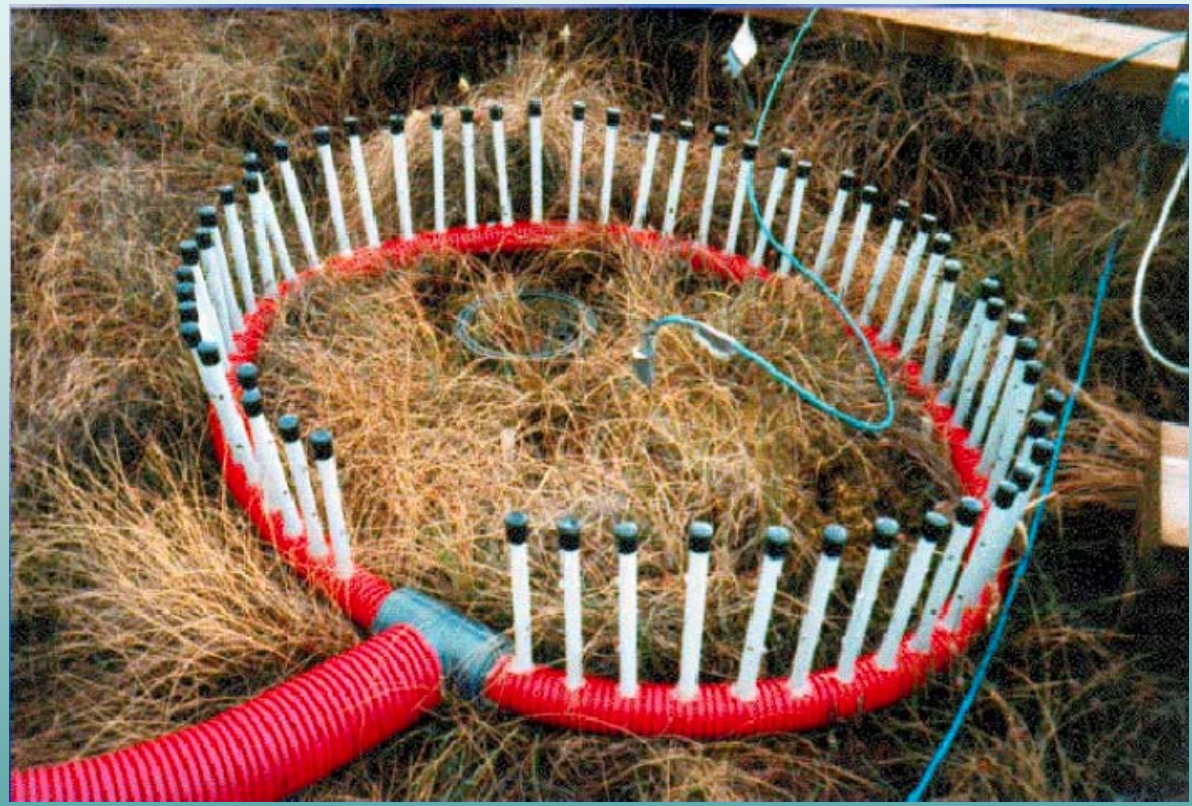
U.S. Dept. of Energy, 1985

It was widely believed that truly open "FACE" systems were impossible. For a forest enrichment of 100 ppm it was calculated that 35,000 tons/yr would be required!

But in 1985 the state of the art was the open top enclosure shown here.

A similar sea-floor enclosure with active baffle controls is feasible, and would permit marine populations to enter and leave, while giving a water residence time sufficient to control ΔCO2. Bill Kirkwood has a design concept that appears elegant and practical

An example of a small-scale system

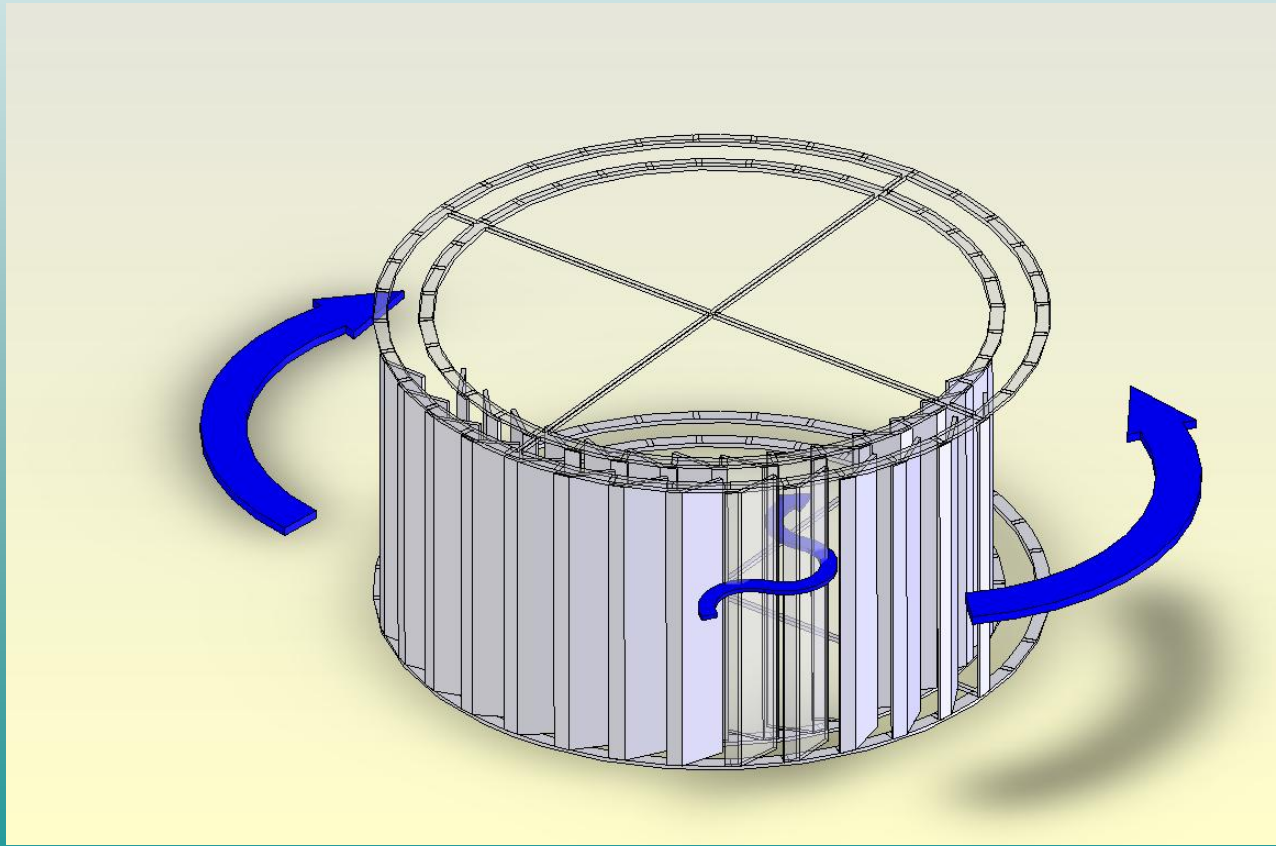


We examined the mini-FACE as one design example; it is the right size, has many flexible emitters for flooding the system, and a large diameter hose – but the delay loop required to supply this is large.

Controlled Flow Concept

Several concepts are being considered for increasing the residence time to reach equilibrium while also reducing the amount of CO2 required, thus greatly enhancing the capability for long term in situ experiments. We can implement the kinetic model into the control algorithm.

Articulated louvers (potentially passive but likely active) allow a controlled volume and velocity of water. Importantly the energy dissipated by flow over these surfaces induces mixing, thus negating the density layering induced by adding the potent fluids.



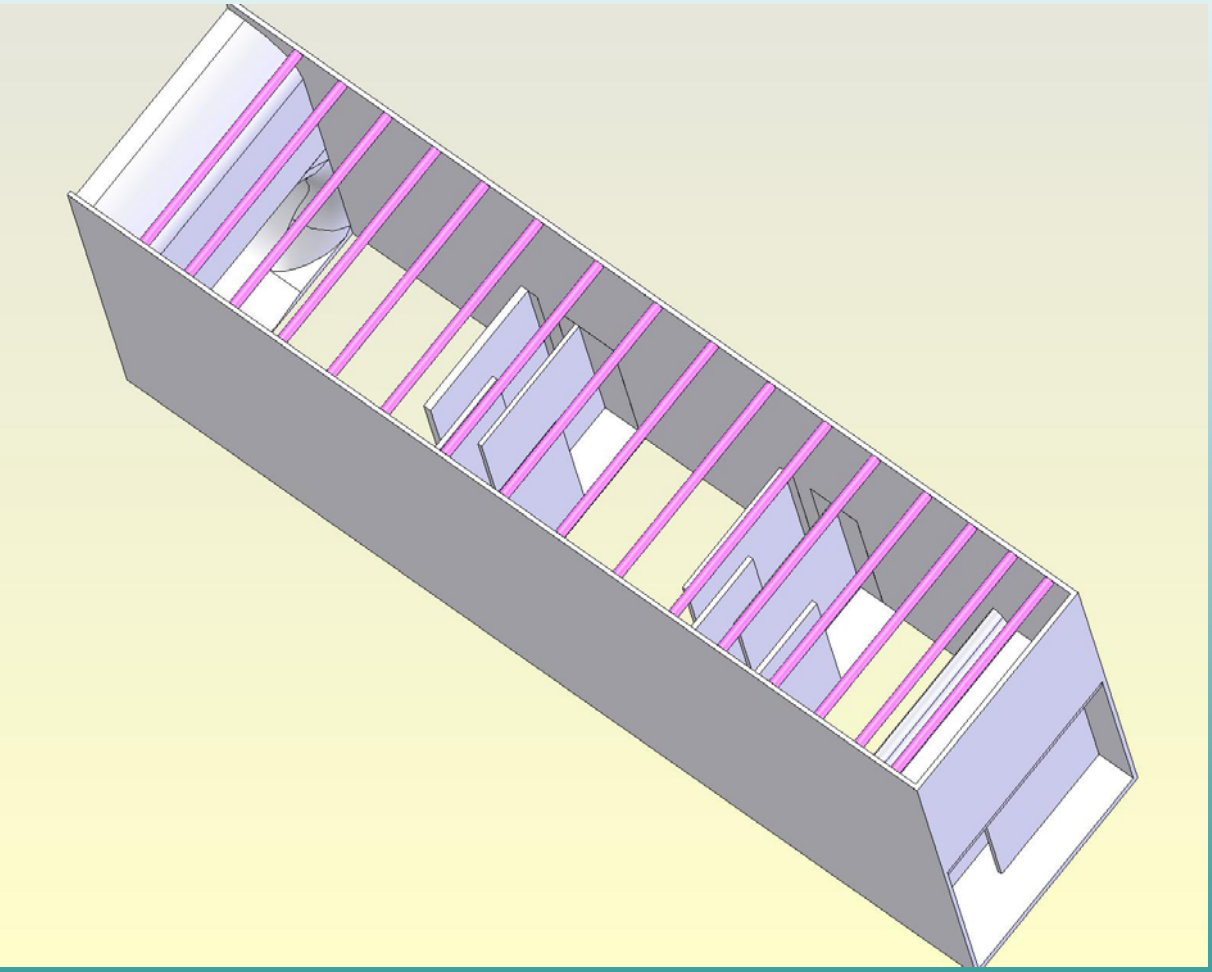
Delivering the CO_2 to the site?

There are four options:

- Delivery of HCl instead of CO2. This has often been used - not the best. It was the procedure for the Biosphere coral experiments.
- Use of CO2 gas – as in the Riebesell team mesocosm experiments. Very precise, but an enclosed system use.
- Delivery of CO2 itself, then reaction with local sea water – problems with hydrate formation in deep, cold systems (below about 400m)
- Formation of a CO2 enriched working fluid on shore, and piped delivery to the site – the best way to proceed for open system studies.

For permit applications it is likely far easier to get permits to deliver CO2 enriched sea water than CO2 itself.

One design concept – flume with forced flow



One design concept – a flume system, with baffles. This allows flow control which can be reasonably matched to natural forcing, open top for deposition and migration. The path length contributes to the required delay time for the H2O-CO2 reaction to occur.

For a 10cm/sec flow rate and a 0.5m x 0.5m cross section then for a 0.3 pH drop we need to deliver about 9.2 kg CO2/day.

This appears to be a very workable design with pump/flow control and drift-free sensors

Summary of Design Issues

There are several critical elements, each of which we have field tested:

- Design of a CO2 enrichment system: Gas/water equilibrator under modest pressure to provide the working fluid.
- Transport of the working fluid to the site
- Dilution of the working fluid with local sea water (~1:1,000) in a mixing chamber
- Creation of a delay loop to allow pH equilibrium to be reached
- Pumping of the ΔpH sea water

Predicting the future? – Let's be careful; these are demanding and complex systems.

The future CO2 scenarios are well debated, but the ocean ecosystem response is not yet well understood. Changes will be slow, intricate, and subtle – and the policy debate may be loud. We should set the bar high for understanding and prediction. Many experiments to date have used very large and not well-constrained enrichments, and modern molecular biological tools have not yet been applied.