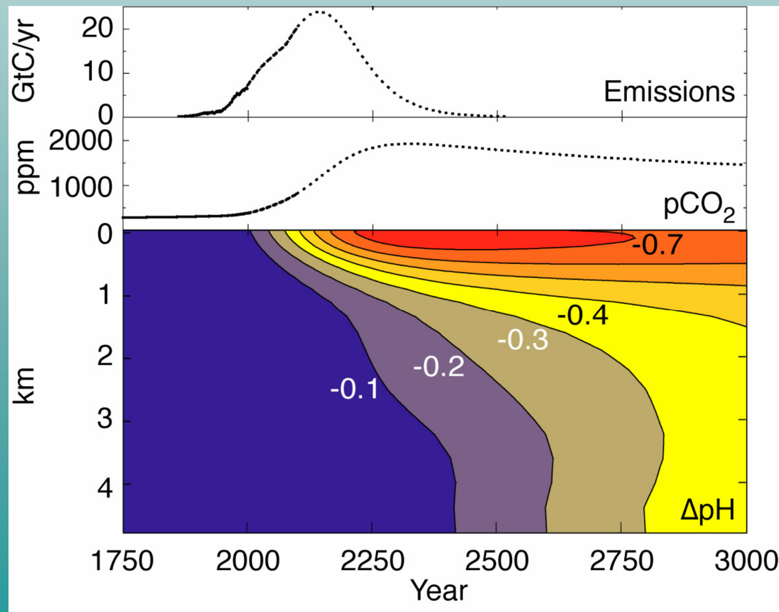
Workshop on the Significance of Changes in Surface CO_2 and Ocean pH in ICES Shelf Sea Ecosystems [WKCpH]

Baden Powell House, London May 2-4, 2007

Peter G. Brewer

Monterey Bay Aquarium Research Institute



WKCpH: Peter G. Brewer (USA) & Liam Fernand (UK) Co-Chairs

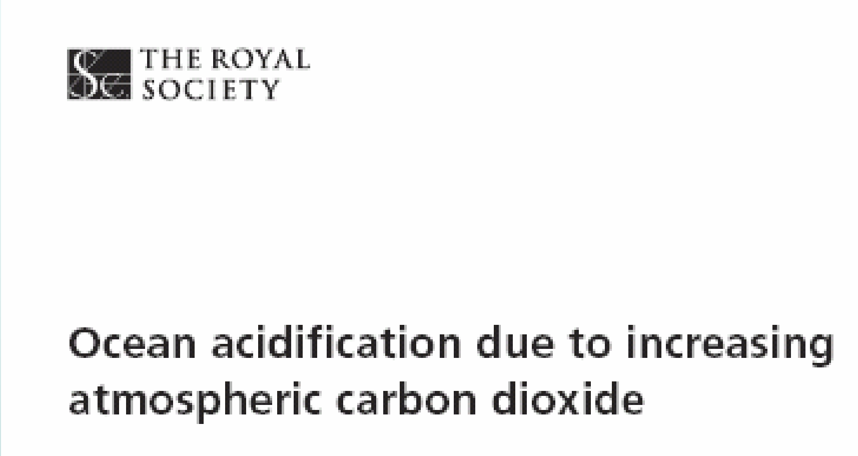
Terms of Reference: Current state of knowledge and future research directions

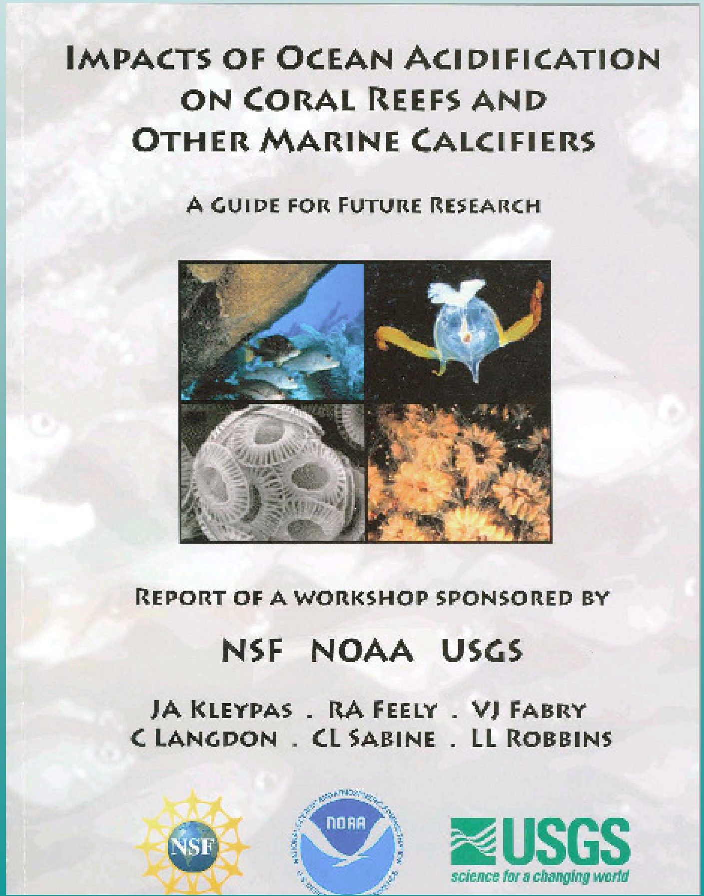
- Spatial and temporal variabilty of surface ocean pH/CO2 in ICES region
- Predict the rates of change and how these can be measured
- Important and relevant pH and CO2 system effects on nutrient chemistry
- Effects of pH and CO2 changes on contaminants

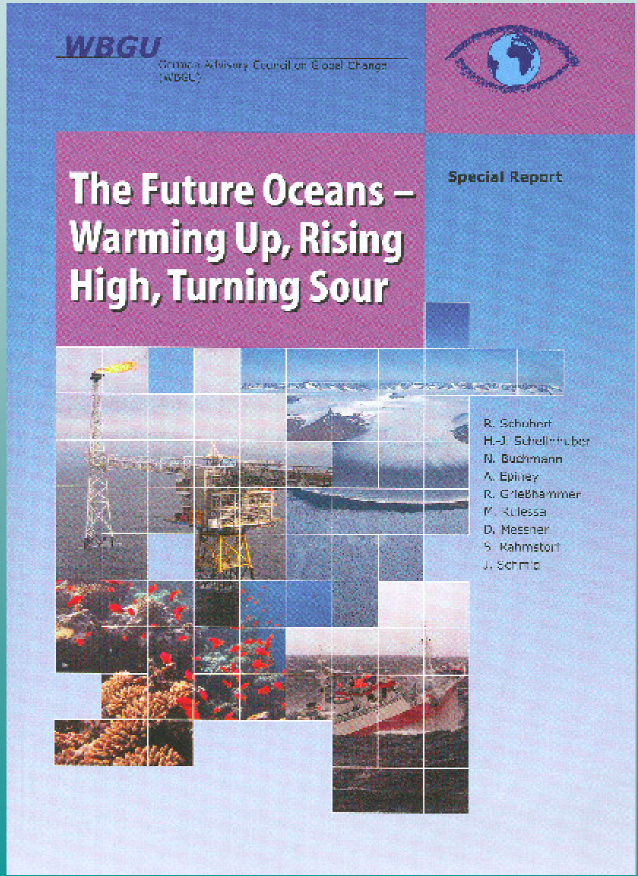
- **Links between changes in pH and effects on marine ecosystem components such as plankton, fish, shell fish, and cold water corals**

There are now many reports on ocean acidification – what drove this?

And how do we move from reports to the practice of science?







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/CO_2 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 CO_2 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 far 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***

Direct Observation of the Oceanic CO_2 Increase

29 years ago - Brewer (1978)

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

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)

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

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.

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.

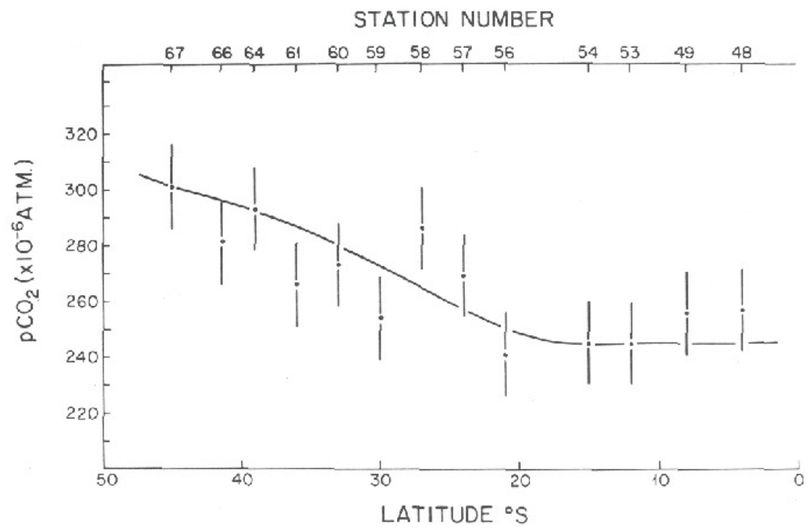


Fig. 2. The calculated initial pCO_2 of samples taken at the core of the salinity minimum of the Antarctic Intermediate Water in 1972.

The fossil fuel CO2 signal is not the only thing forcing large ocean pH changes

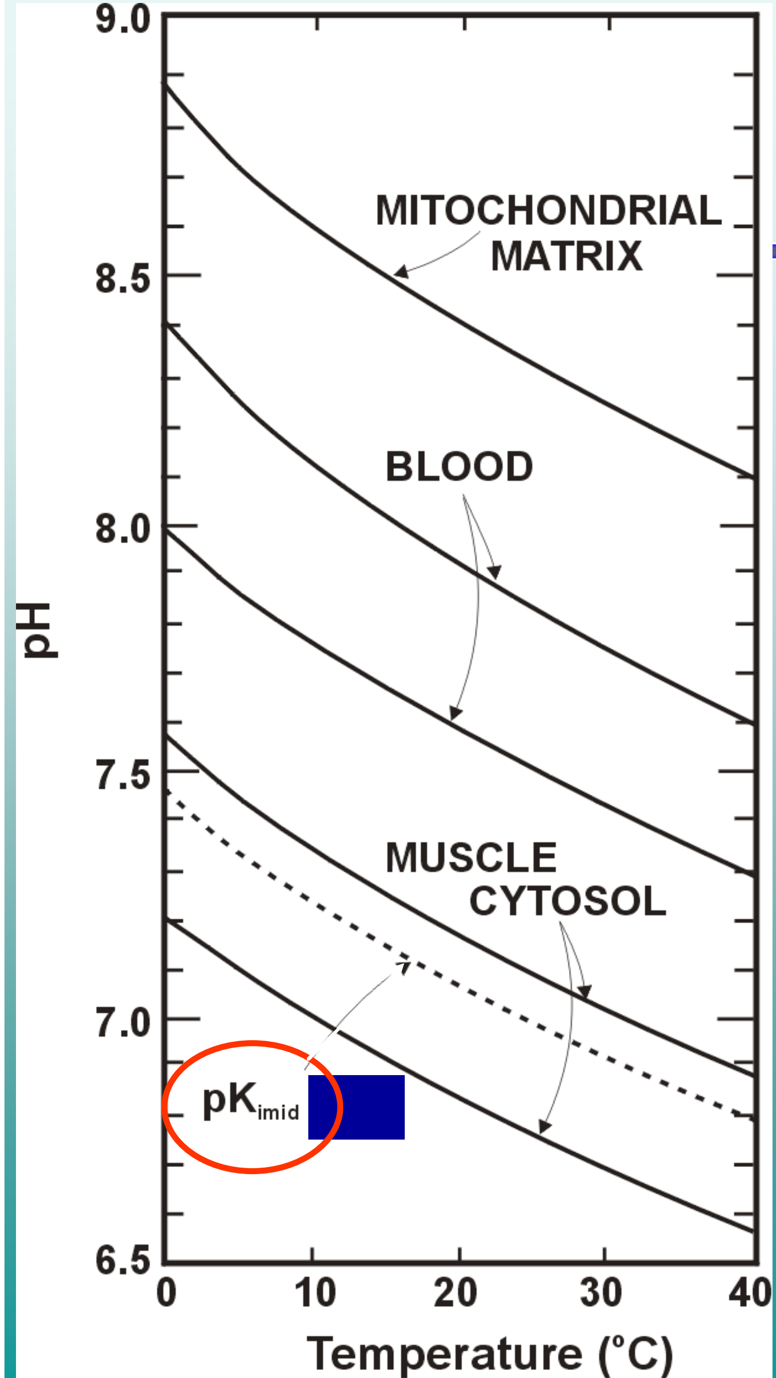
Changing ocean pH/CO_2 is one additional stress imposed on marine ecosystems in shelf seas – but it is a global one, and of very long duration. It is additive to thermal and O2 deficiency stress: these changes are correlated.

Climate Change Affects Marine Fishes Through the Oxygen Limitation of Thermal Tolerance

Hans O. Pörtner* and Rainer Knust

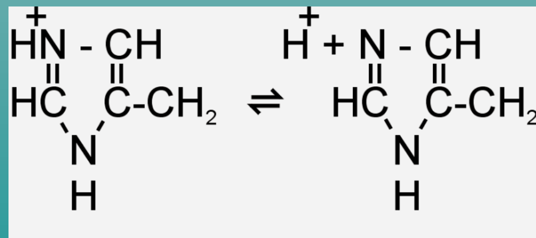
A cause-and-effect understanding of climate influences on ecosystems requires evaluation of thermal limits of member species and of their ability to cope with changing temperatures. Laboratory data available for marine fish and invertebrates from various climatic regions led to the hypothesis that, as a unifying principle, a mismatch between the demand for oxygen and the capacity of oxygen supply to tissues is the first mechanism to restrict whole-animal tolerance to thermal extremes. We show in the eelpout, *Zoarces viviparus*, a bioindicator fish species for environmental monitoring from North and Baltic Seas (Helcom), that thermally limited oxygen delivery closely matches environmental temperatures beyond which growth performance and abundance decrease. Decrements in aerobic performance in warming seas will thus be the first process to cause extinction or relocation to cooler waters.

From: Portner and Knust, 2007



Conserving charge states of proteins

- **pH** falls by approx. 0.02 per a 1°C rise in body temperature
- **pK of histidine imidazole** sidechain (pK_{imid}) varies identically
- *Ergo*: **dissociation state of imidazole sidechains remains stable as temperature (& pH) vary.**



Histidine Imidazole

Oceanic oxygen levels have been on the decline for some time:

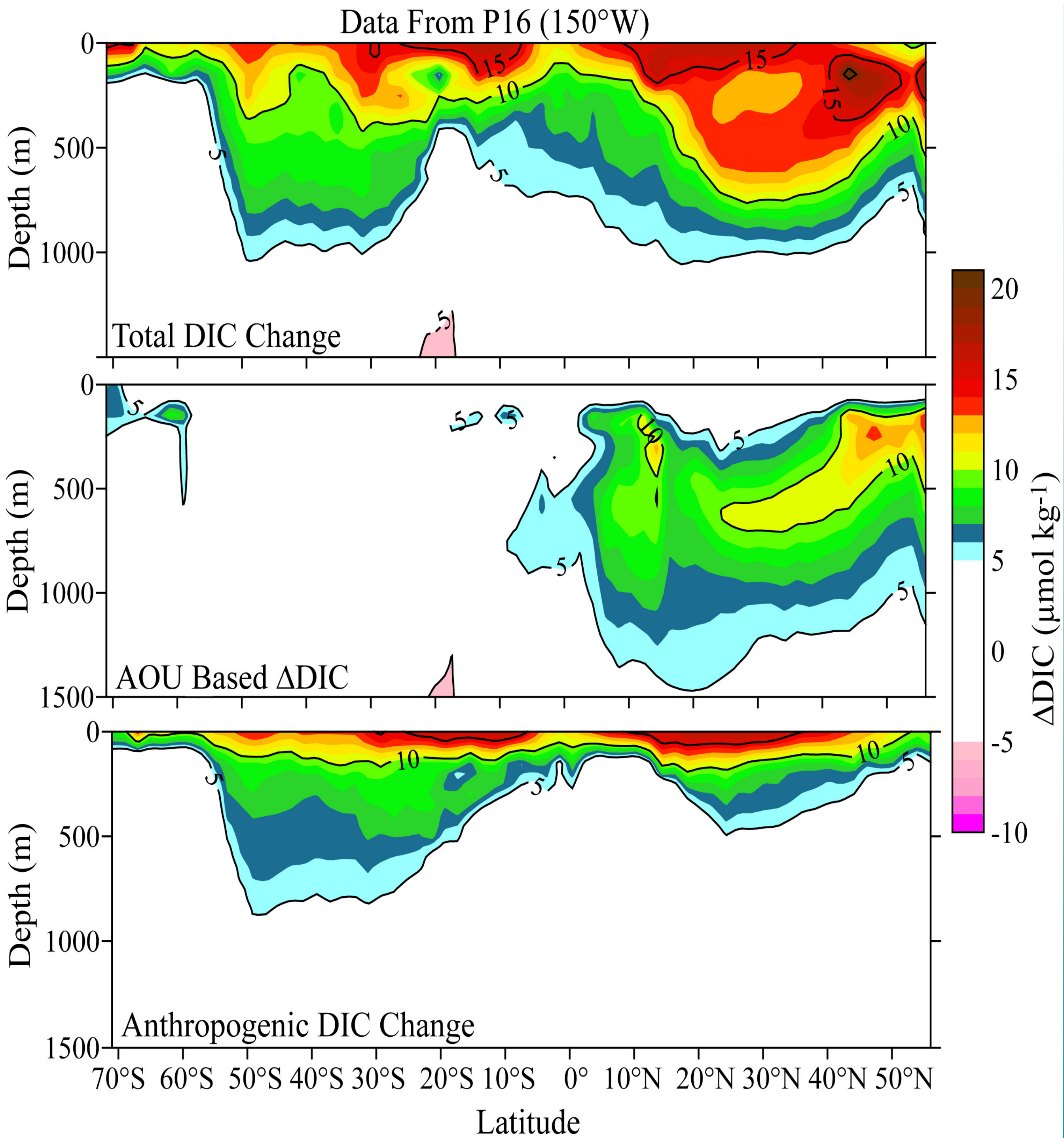
- Trends to anoxia first detected in the Baltic early in the 20th century – and the deep basins are now permanently anoxic
- Seasonally anoxic waters appeared on the shelf off New Jersey beginning in the 1980s
- Large-scale seasonal anoxia now occurs in the shallow Gulf of Mexico
- Seasonally anoxic waters appeared off Oregon in 2005
- Trends to anoxia are readily detectable in the Sea of Japan:

An anoxic Sea of Japan by the year 2200?

C.T.A. Chen [a,*], A.S. Bychkov [b], S.L. Wang [a], G.Yu. Pavlova [b]

[a] *Institute of Marine Geology and Chemistry, National Sun Yat-sen University, Kaohsiung 804, Taiwan*
[b] *Pacific Oceanological Institute, Vladivostok, Russian Federation*

The global pH trend from fossil fuel CO2 is additive to the regional O2/CO2 stresses – the fossil fuel CO2 calculation discards the O2 related trends. We likely under-estimate the total pH shift.



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)

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

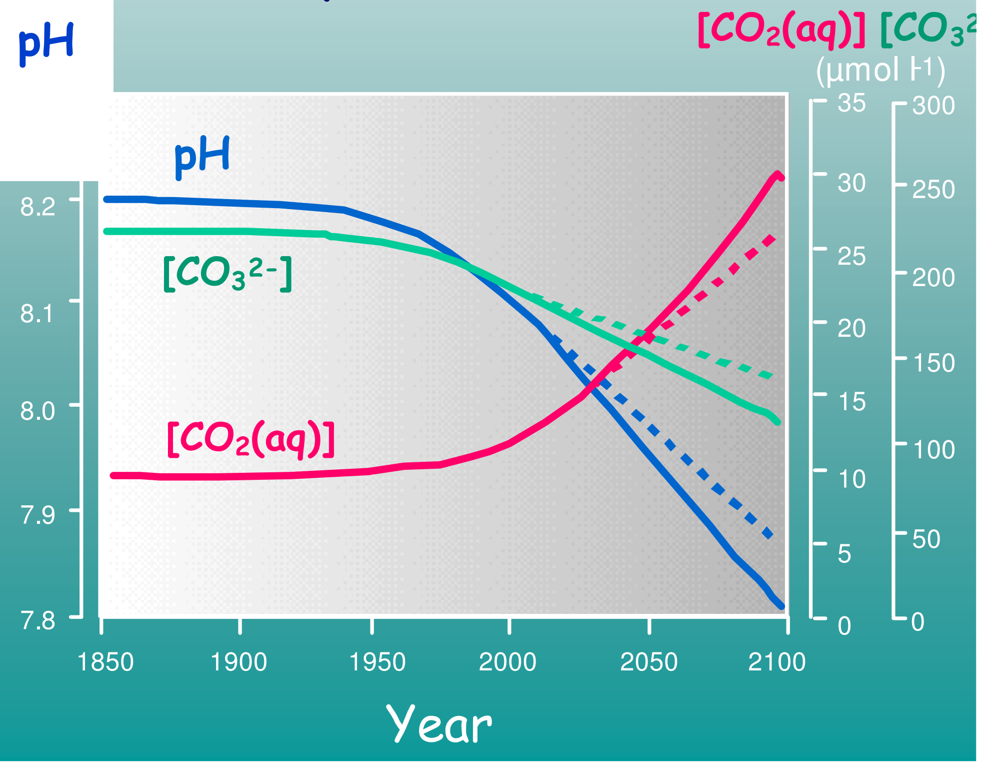
Time	pCO_2	Total CO_2	pH	HCO_3^-	CO_3^{2-}	H_2CO_3
yr.	µatm	µmol kg^{-1}		µmol kg^{-1}	µmol kg^{-1}	µmol kg^{-1}
1800	280	2017	8.191	1789	217	10.5
1996	360	2067	8.101	1869	184	13.5
2020	440	2105	8.028	1928	161	16.5
2040	510	2131	7.972	1968	144	19.1
2060	600	2158	7.911	2008	128	22.5
2080	700	2182	7.851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

From Brewer 1997

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



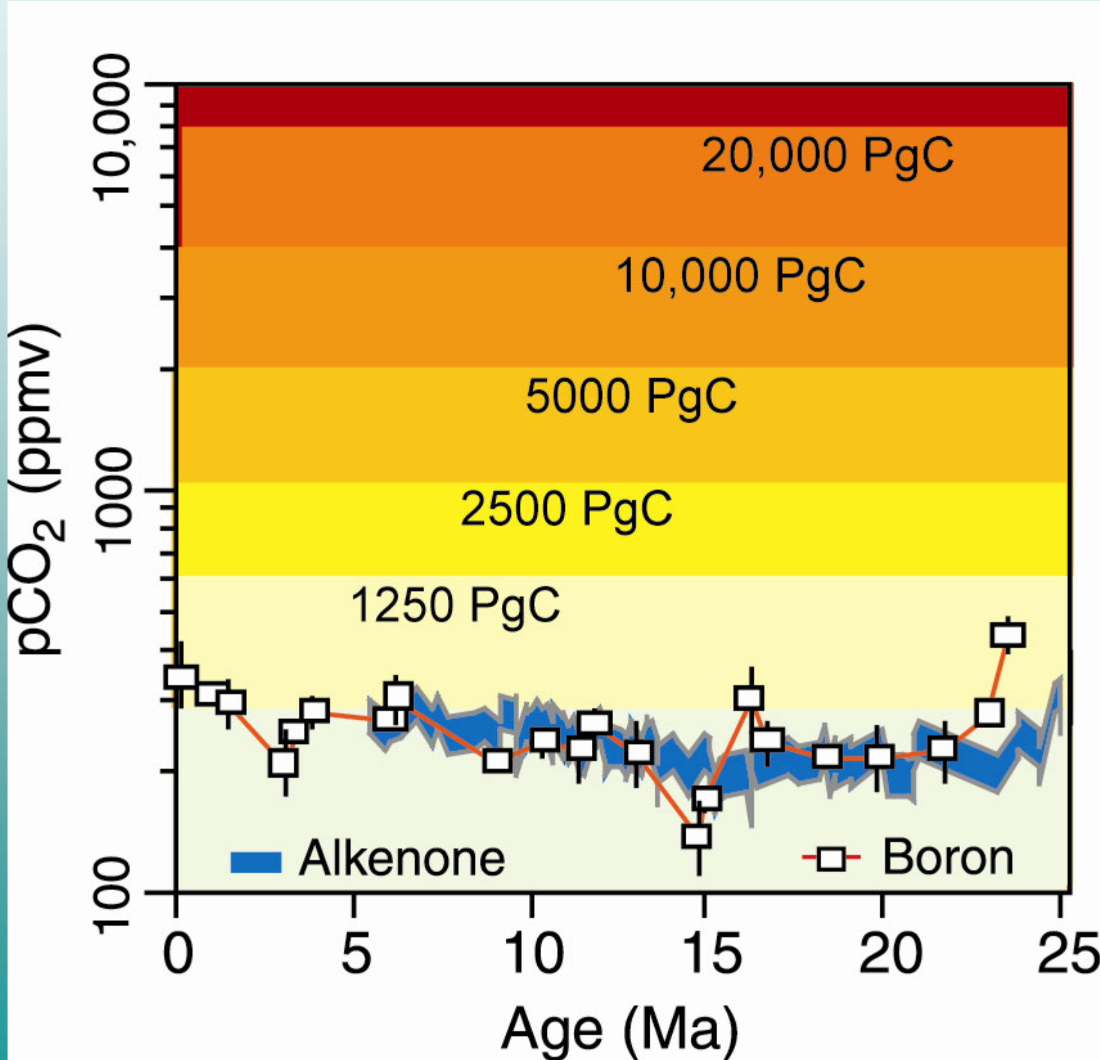
The log scale for pH often confuses the lay person. The drop in carbonate ion, and indicator of ease of formation of carbonate skeletons, will be dramatic

Predicted future CO_2 concentration exceed those inferred for past 25 million years

Even if most fossil-fuel carbon is never released to the atmosphere, we will produce geologically unusual conditions

Paleo-CO_2 [lines]
(Zachos et al., 2001)

Year 2300 atmospheric CO_2 predictions for scenarios involving fossil-fuel plus net biomass release over several centuries [colors]
(Caldeira and Wickett, 2005)



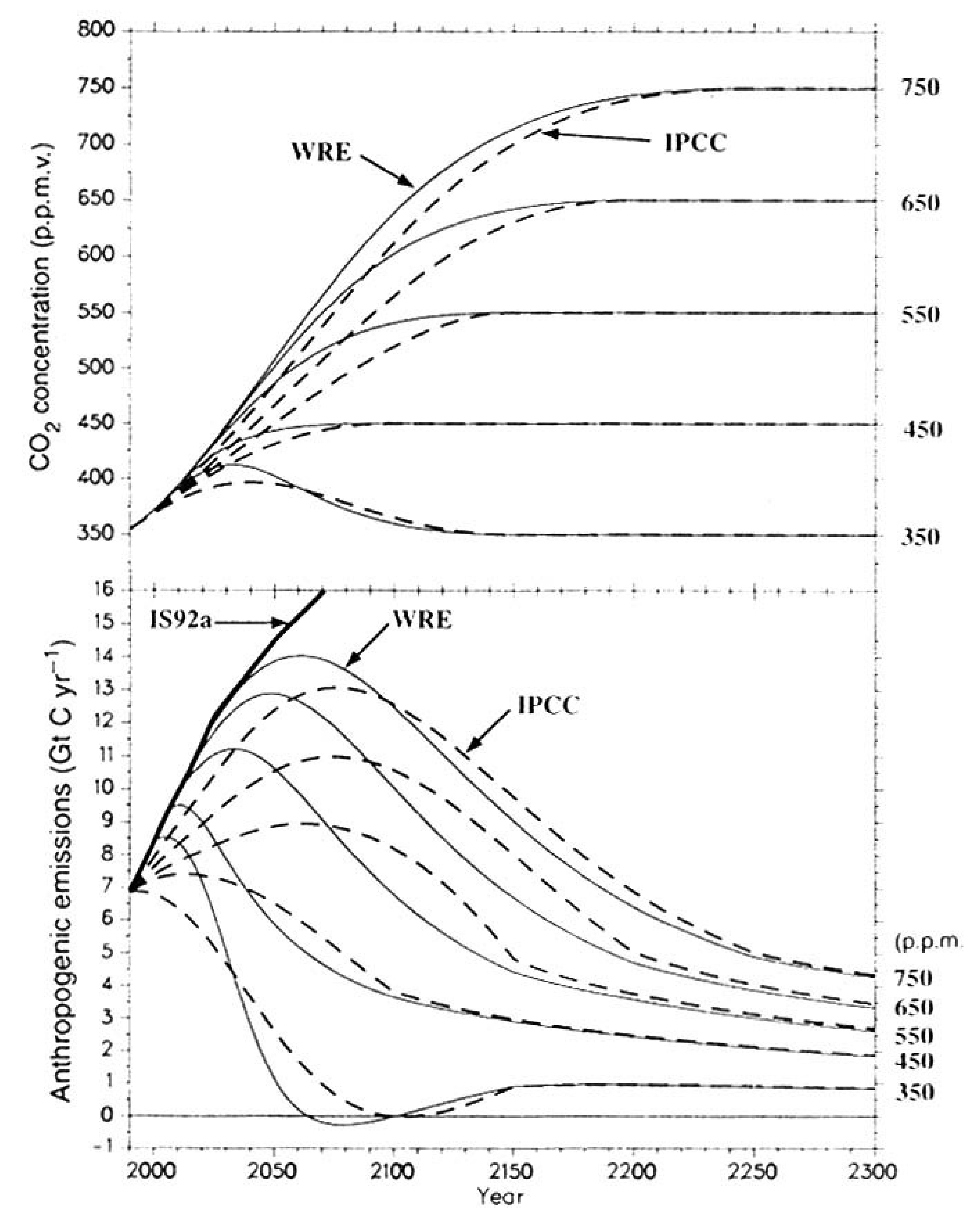
Some examples from earth history over the last 100M years

(i) The seven glacial-interglacial transitions of the last 650,000 years, where atmospheric CO2 repeatedly increased by up to 100 ppm (40%), accompanied by a surface ocean pH decrease of the order of 0.15 units.

(ii) The Eocene change in carbonate compensation depth.

(iii) The Paleocene Eocene Thermal Maximum 55 million years ago, where abrupt processes (e.g. massive release and oxidation of methane hydrates) resulted in a transient CO2 increase of the order of several hundred ppm, presumably at a high rate that approximates the present situation. This event also provides the opportunity to observe recovery times of the earth system to a CO2 perturbation.

(iv) The middle Cretaceous ~100-80 million years ago as an example of an extreme and lasting Greenhouse world with estimated atmospheric CO2 concentrations three to ten times higher than present.



From Wigley et al. (1996)

Emission trajectories required to achieve stabilization of atmospheric CO_2 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 CO_2 per year are required by 2025, and about 14.7 billion tons per year by 2050.

The long “tail” is controlled by the 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

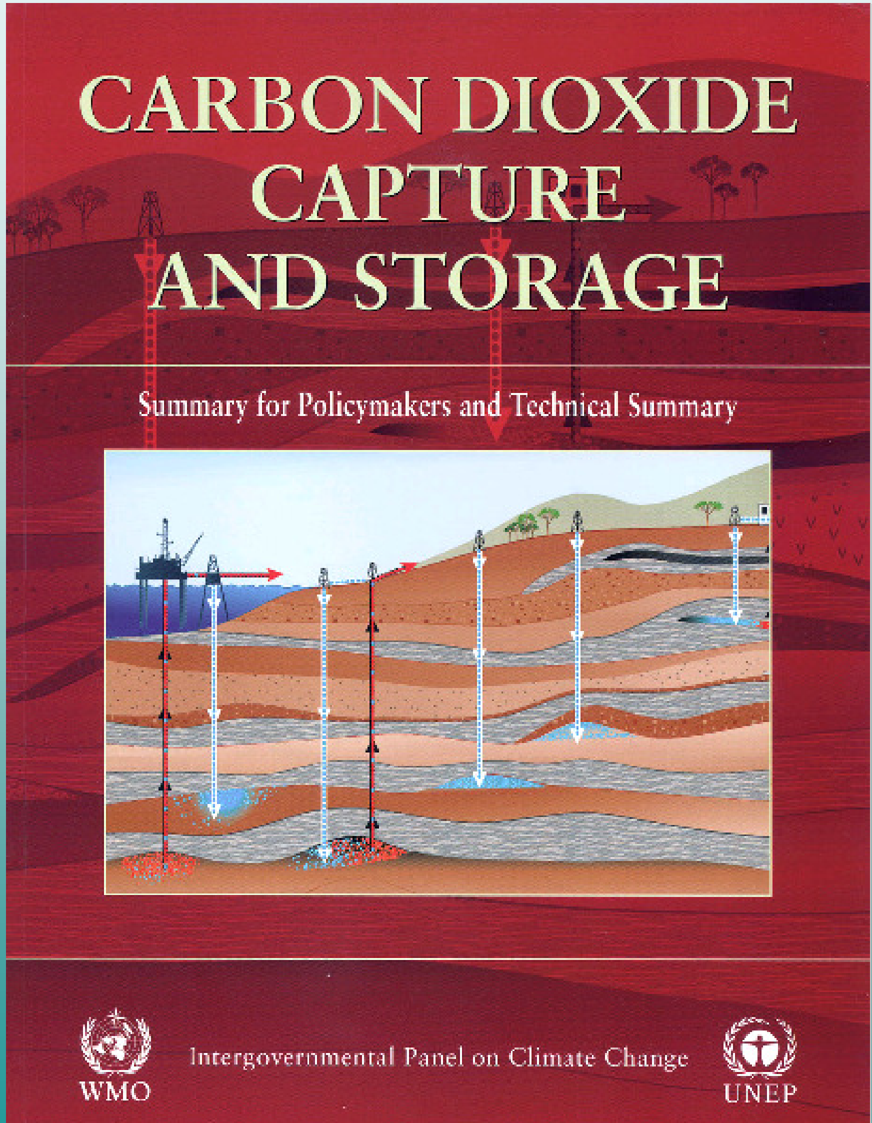
An early ocean CO_2 sequestration experiment
(Brewer et al. 1999)

The bold and successful execution of this 4 L scale experiment galvanized interest in ocean CO2 issues in a way that a graph showing billions of tons did not. Such is the power of image.

Large natural sea floor CO2 vents have since been discovered.

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.

Ocean scientists have already had a remarkable influence in policy in the CO_2 sequestration area



The rapidly advancing ability of ocean scientists to execute technically advanced experiments at sea has already greatly influenced important international studies on CO_2 policy.

One example is seen with the recent IPCC report to the UNFCC. This makes it clear that at stabilization of 650 ppm CO2 the limit will be reached when the ocean has absorbed some 7.5 trillion tons of CO2. At that point air and sea will be at equilibrium – and zero fossil fuel emissions would be allowed. This may be an impossible goal for mankind in an industrial society.

The CO2 capture process robs a power plant of about 30% of its energy - and the environmental footprint is large

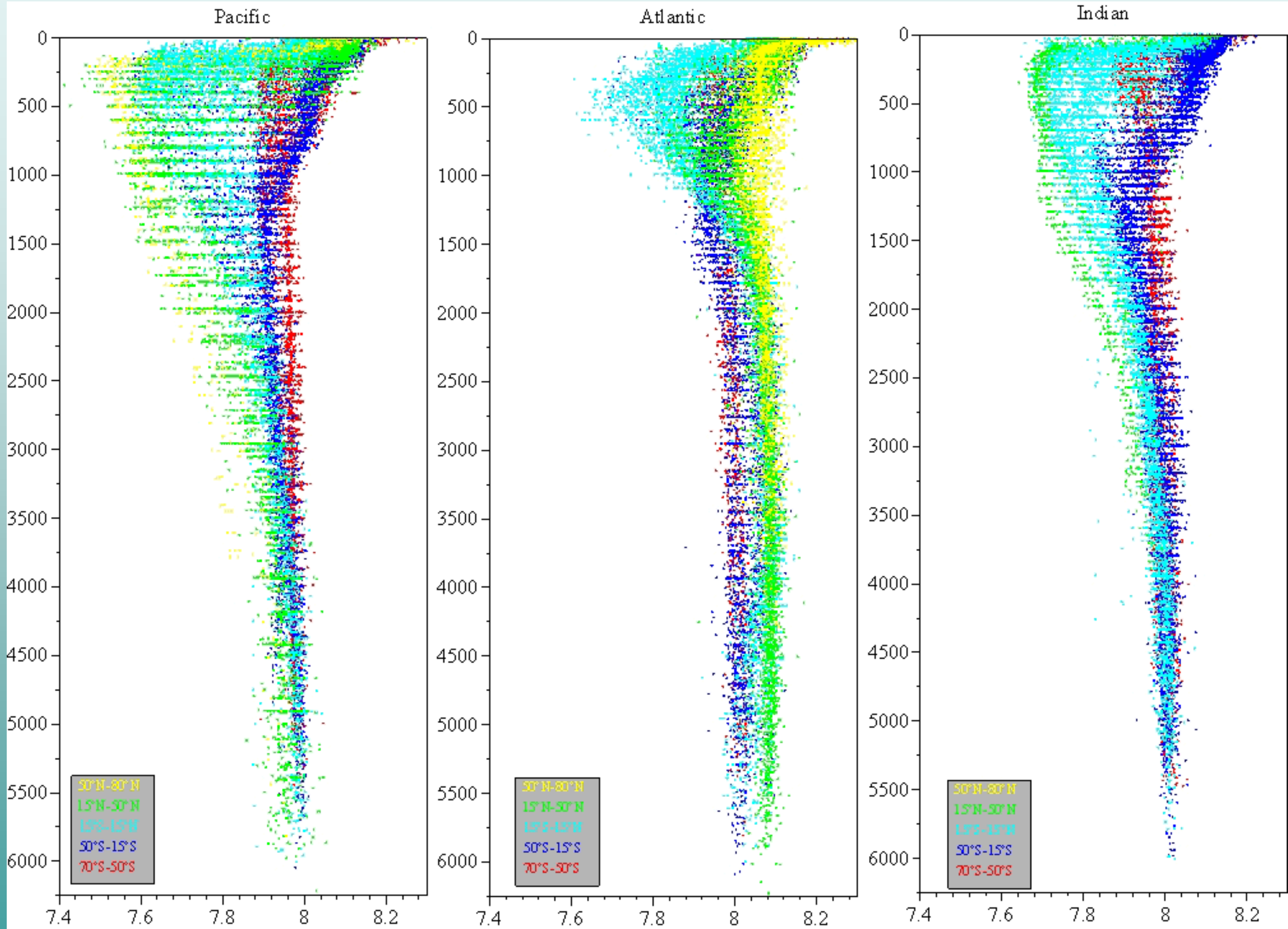
The CO_2 capture process involves large scale industrial activity with a significant environmental footprint. The 4 contacting towers in the plant at right are for the North Dakota CO_2 capture facility.

(a)

(b)

Observed variation in open ocean pH for the 1990s (total hydrogen scale; data from GLODAP data set, Key et al., 2004).

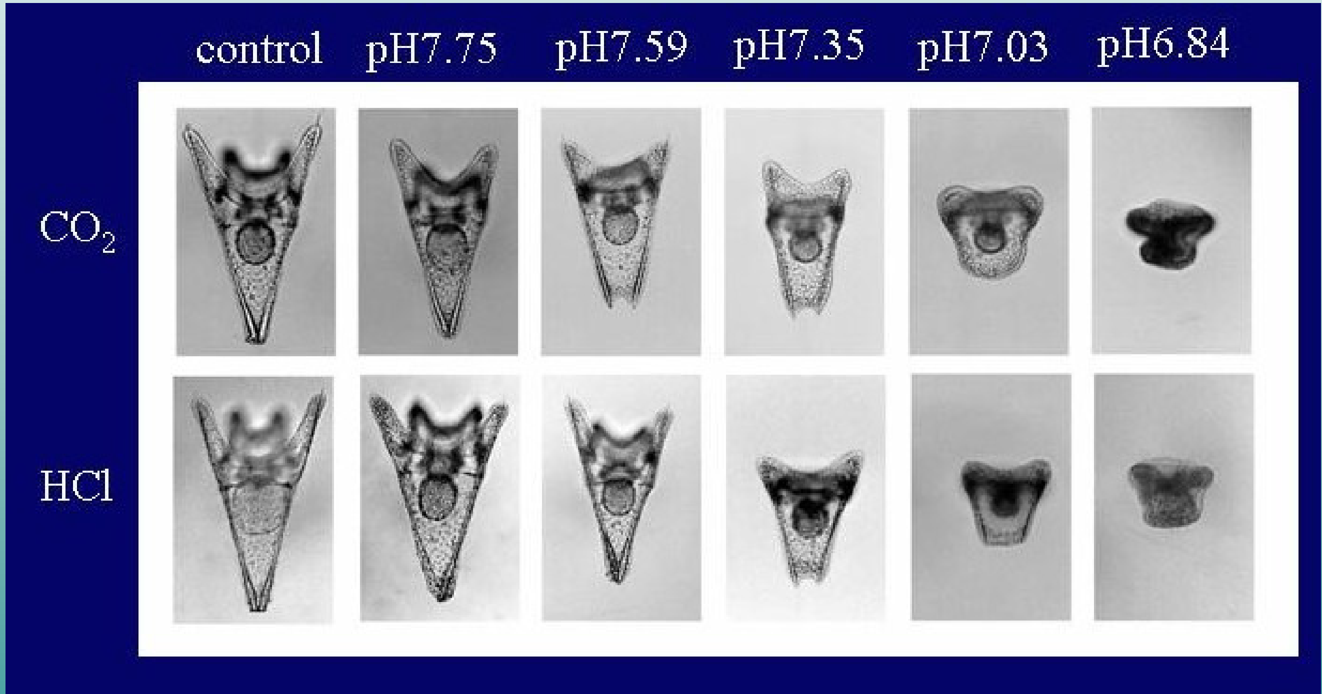
Pre-industrial surface values were about 0.1 pH units greater than in the 1990s.



Waters off Monterey are some of the lowest pH in the world ocean; a change of 0.4 pH or greater would shift the entire ocean to these extreme values – and our local waters to values not seen in millions of years.

It is now widely believed that the high CO_2/low pH effects will impact marine systems in a variety of ways

The example below is taken from the work of Shirayama et al., showing effects of CO_2 on sea urchin reproduction. In fact very few well qualified studies yet exist.



There have been many experiments using acid to lower pH. It is very likely that only direct CO2 addition will yield satisfactory results, so these skills will be essential.

Are there key indicator organisms from which we may draw general conclusions?

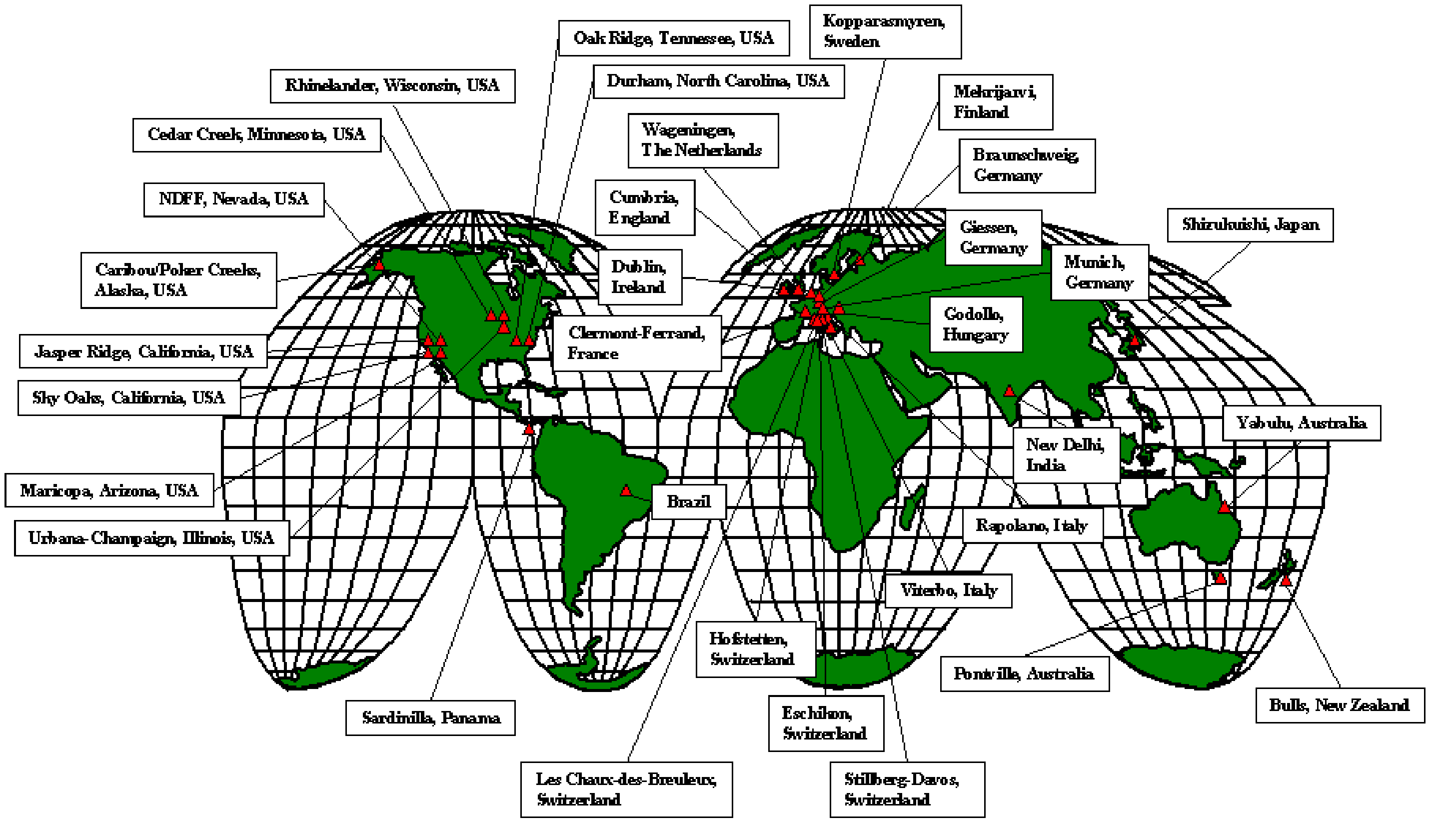
The extensive work on ocean acid disposal in the 1970s showed that zooplankton reproduction was the most sensitive component of the ecosystem. Is it possible that the most sensitive stage will be embryonic/juvenile forms?

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

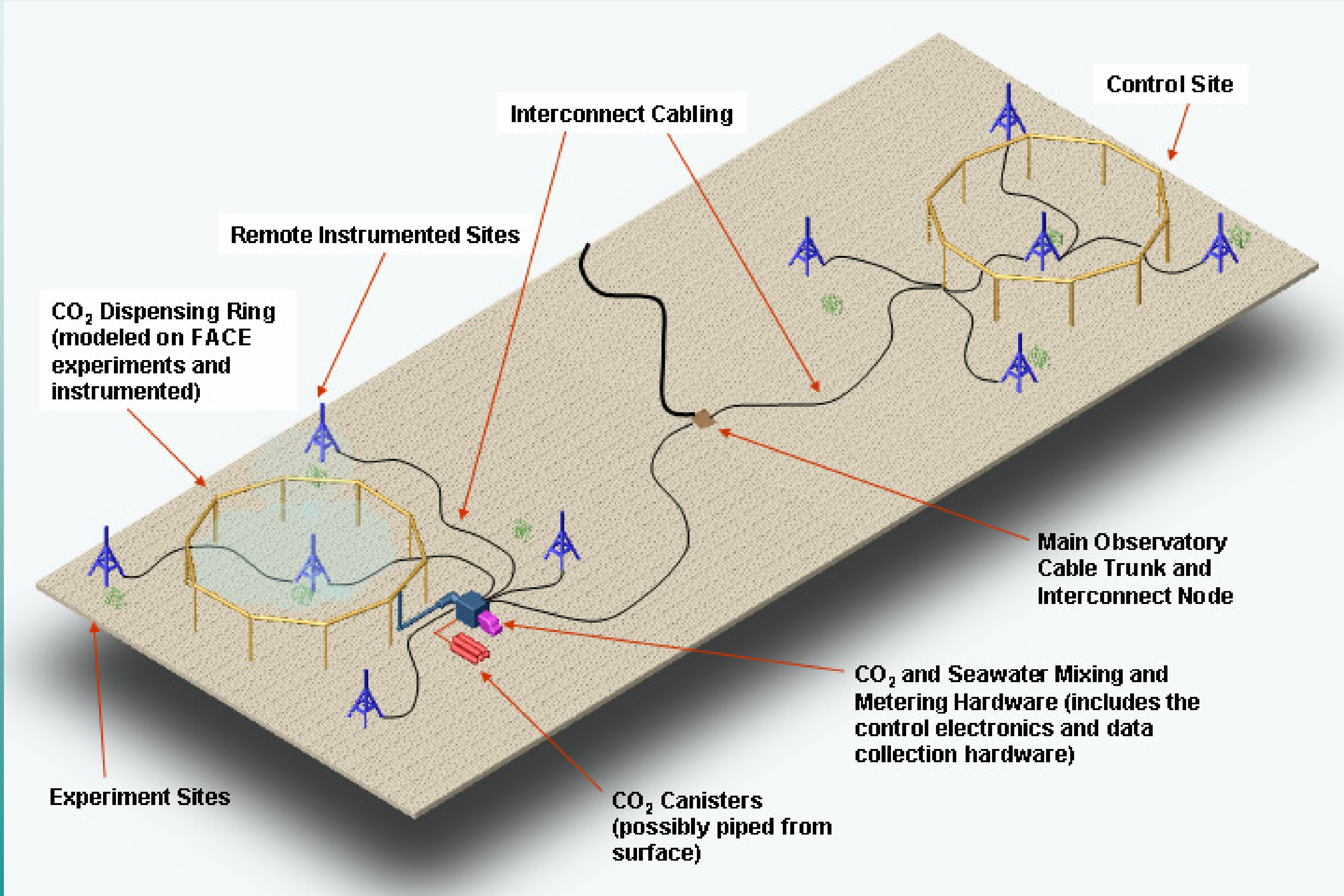
Recent work shows that claims of land plant fertilization from higher CO2 levels have been overstated by ~50%. The early work on enclosures is undone by truly open experiments. How well can we predict oceanic effects with today's techniques?

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

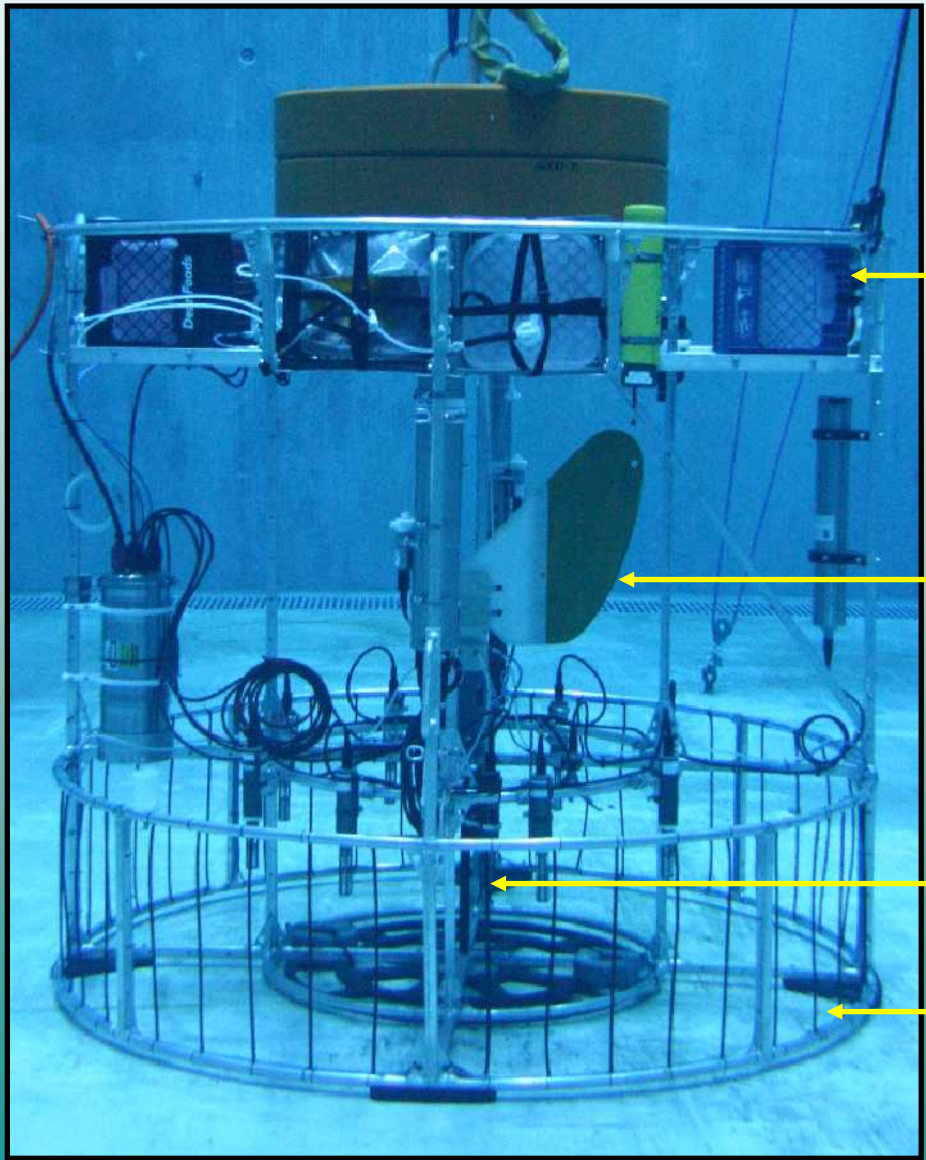
Stephen P. Long,[1,2,3*] Elizabeth A. Ainsworth,[4,1,3] Andrew D. B. Leakey,[3,1] Josef Nösberger,[5] Donald R. Ort[4,1,2,3]

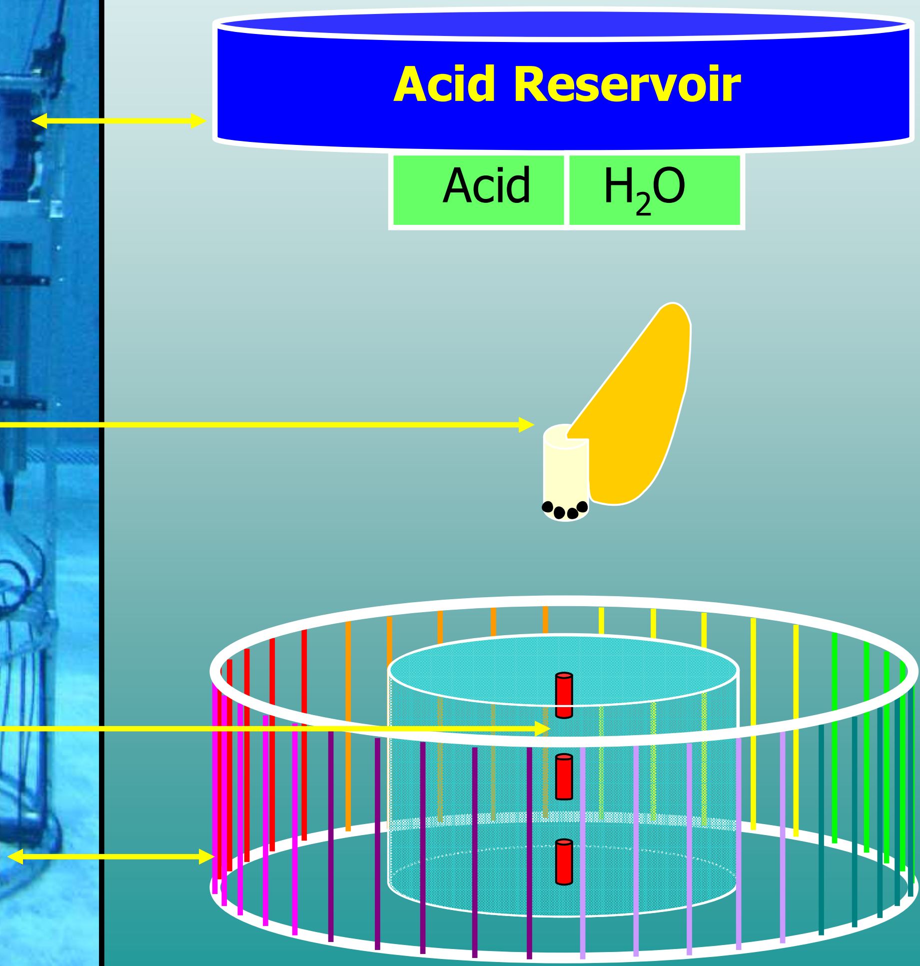
Model projections suggest that although increased temperature and decreased soil moisture will act to reduce global crop yields by 2050, the direct fertilization effect of rising carbon dioxide concentration ($[CO_2]$) will offset these losses. The CO_2 fertilization factors used in models to project 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



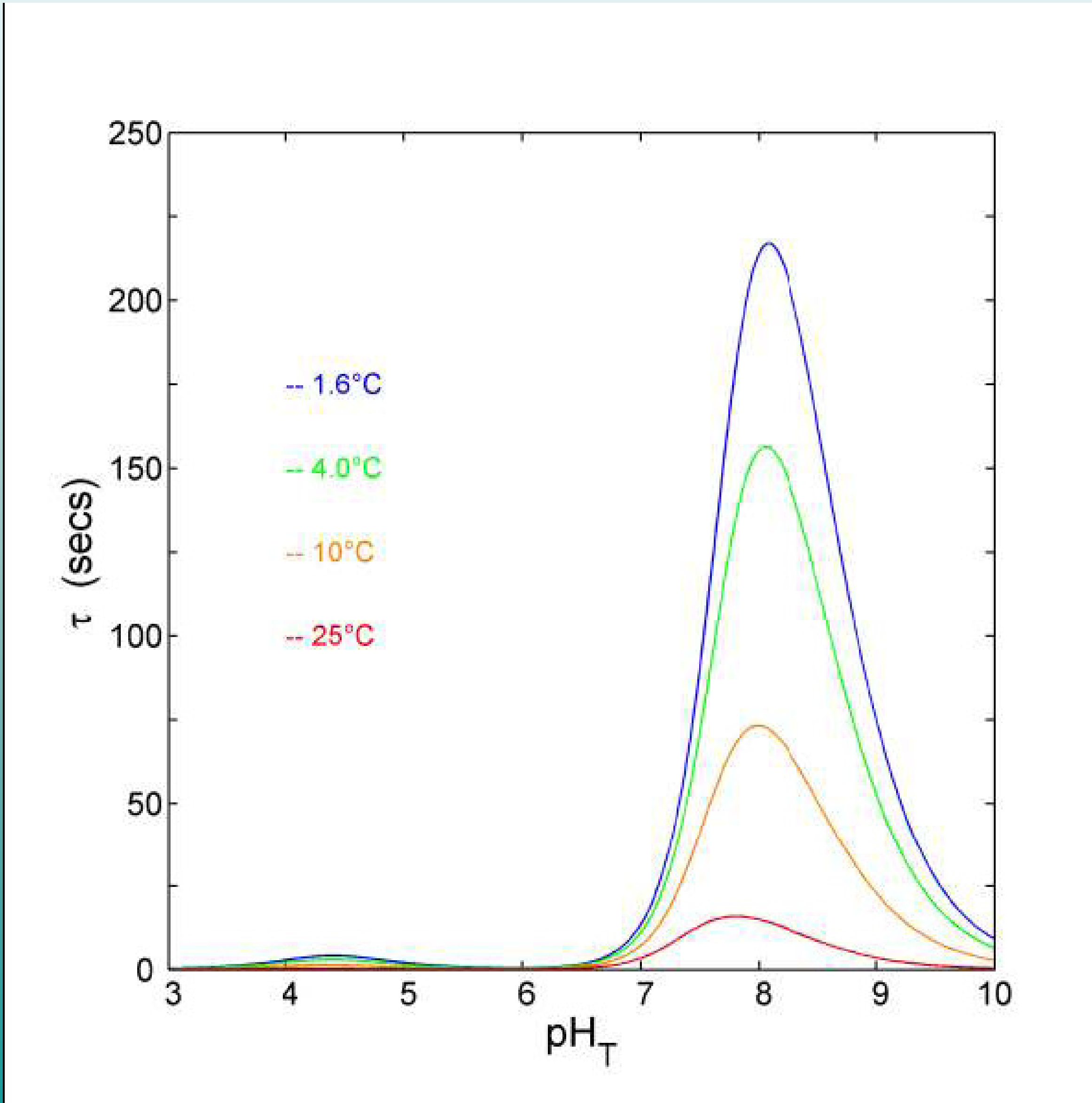
The FOCE Prototype – a double ring with acid emitters and sophisticated valve control to allow for system latency





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.

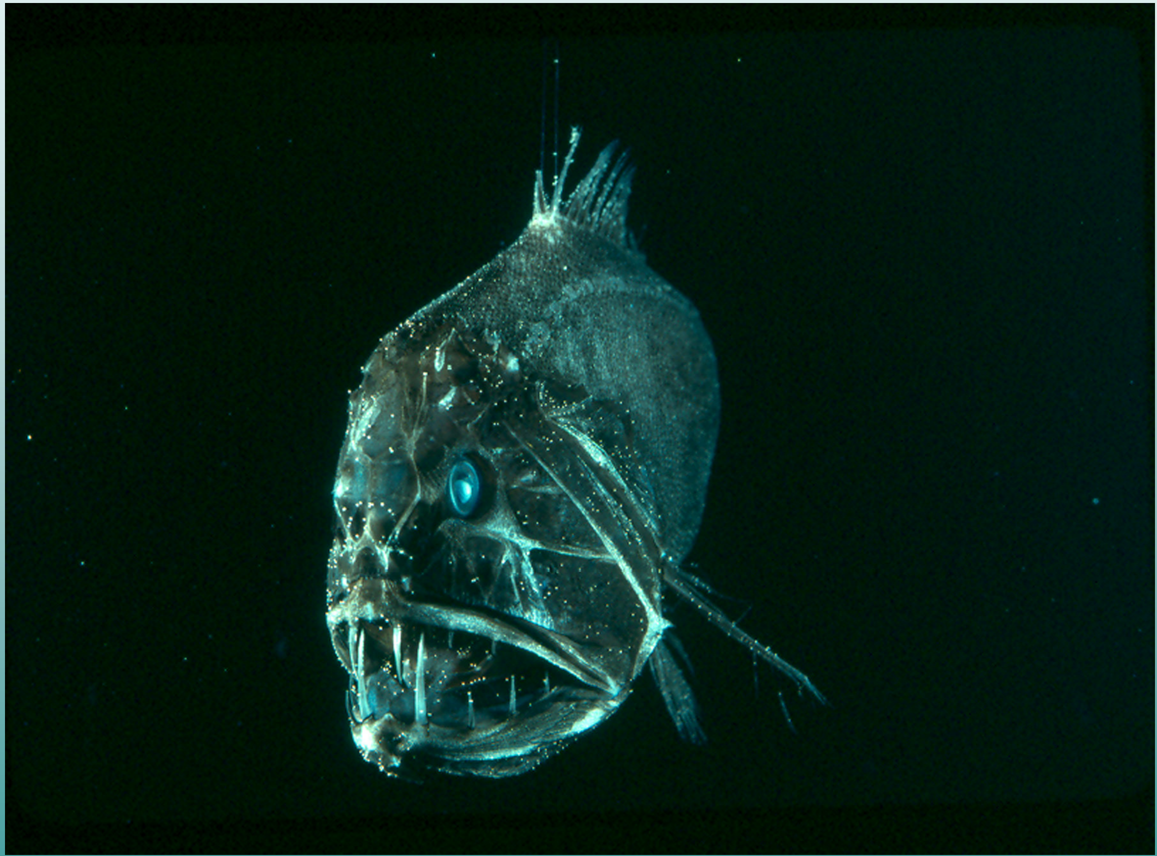
For warm surface water (coral reef) experiments a residence time in the perturbation area of about 2 minutes is required for significant equilibration. Cold, deep waters are lower pH and the residence times are longer.

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.

MBARI has outstanding skills in mid-water ROV observations



Fangtooth as an example

Many mid-water animals inhabit some of the lowest pH waters in the world ocean – high CO_2 and low O_2. How will they cope with an ocean of far higher CO_2 levels in the future?

While returning the animals to the surface for experiment is the standard way, this does present some artifacts, and development of in situ exposure and sampling methods would be an important breakthrough.

Challenges of creating an *in situ* chemostat

- *Control and Recovery*

- *By containing an animal in an enclosed vessel we initiate loss of oxygen, and increase of CO_2, from respiration.*
- *We can reduce pH/elevate CO_2 by direct injection, but then have to maintain the condition set*
- *This means removing the CO_2 respired, and adding O_2 in a carefully controlled manner.*
- *We can likely lower CO_2 by bleeding in background sea water, and adding O_2 by injection of O_2 rich sea water*
- *For simulation of the late 21st century ocean we should also raise temperature by 2 - 4°C, and maintain this.*
- *After some time the animal will adjust to the new environmental state, expressing this as physiological change*
- *This will change will be expressed at the molecular level, which must then be sampled, preserved and recovered*
- *"Normal" procedure is to drop the animal into liquid N_2 – we can't do this in situ*
- *Some other mechanism of signal preservation will have to be developed*

What calcifying ecosystems are at risk?

Reefs of the Deep: The Biology and Geology of Cold-Water Coral Ecosystems

J. Murray Roberts,[1] Andrew J. Wheeler,[2] André Freiwald[3]

Coral reefs are generally associated with shallow tropical seas; however, recent deep-ocean exploration using advanced acoustics and submersibles has revealed unexpectedly widespread and diverse coral ecosystems in deep waters on continental shelves, slopes, seamounts, and ridge systems around the world. Advances reviewed here include the use of corals as paleoclimatic archives and their biogeological functioning, biodiversity, and biogeography. Threats to these fragile, long-lived, and rich ecosystems are mounting: The impacts of deep-water trawling are already widespread, and effects of ocean acidification are potentially devastating.

With the re-discovery of deep cold water corals there has been a strong move to protect these ecosystems. How real is the CO_2 threat to, for example, Davidson Seamount? – There have been calcifying organisms on earth for a very long time.

Sea mounts are well recognized as areas of prolific coral growth

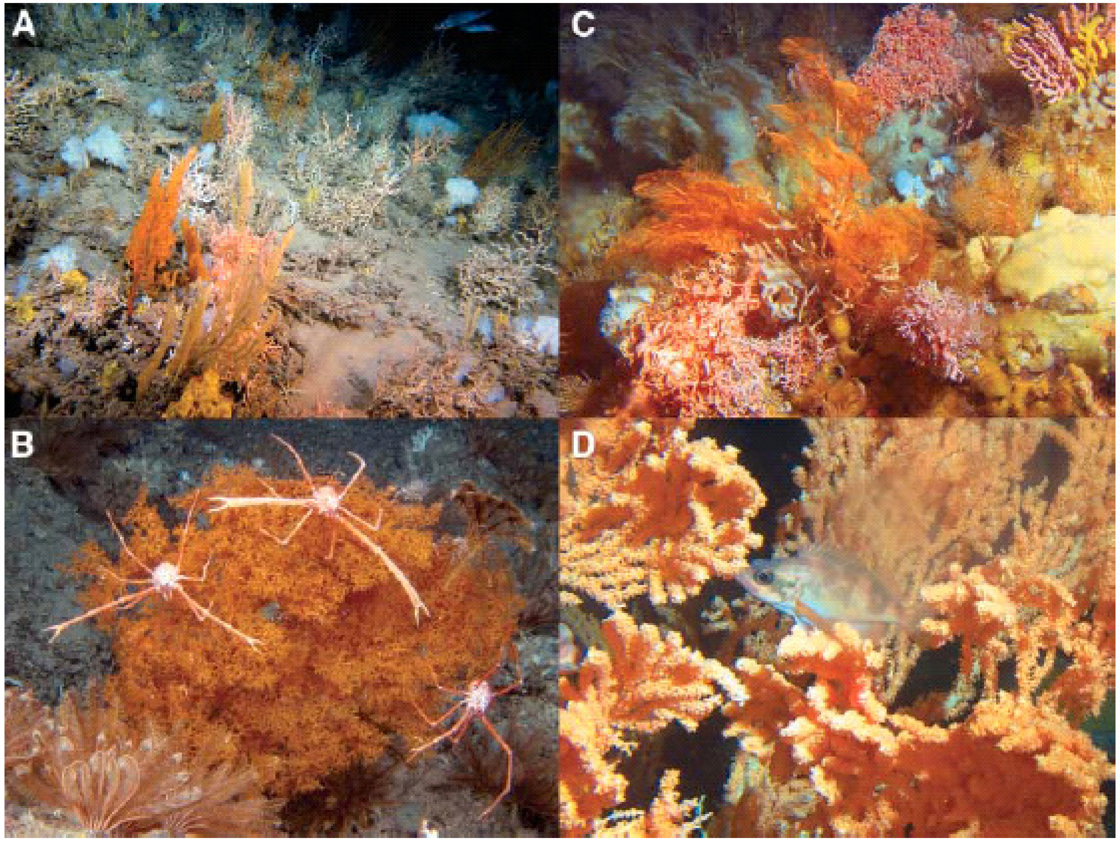


Fig. 1. Cold-water coral reef fauna. (**A**) Sloping flank of the Galway carbonate mound colonized by scleractinian and gorgonian corals and glass sponges. (**B**) Currently undescribed antipatharian coral (*Leiopathes* sp., pers. comm. D. Opresko) and associated anomuran crustaceans from the Twin Mounds, Porcupine Bank (NE Atlantic). [Images courtesy Alfred-Wegener-Institut für Polar und Meeresforschung and Institut Français de Recherche pour l'Exploitation de la Mer] (**C**) Diverse coral and sponge fauna recently discovered off the Aleutian Islands. [Image courtesy of A. Lindner, National Oceanic and Atmospheric Administration (NOAA) Fisheries] (**D**) Sharpchin rockfish (*Sebastes* sp.) among gorgonian corals (*Primnoa* sp.) in the Gulf of Alaska (N Pacific). [Image courtesy of V. O'Connell, Alaska Department of Fish and Game]

From Roberts et al., 2005

An ensemble of cold water coral systems. Davidson seamount off our coast is one well known example explored by MBARI and the Sanctuary. Is this system threatened?

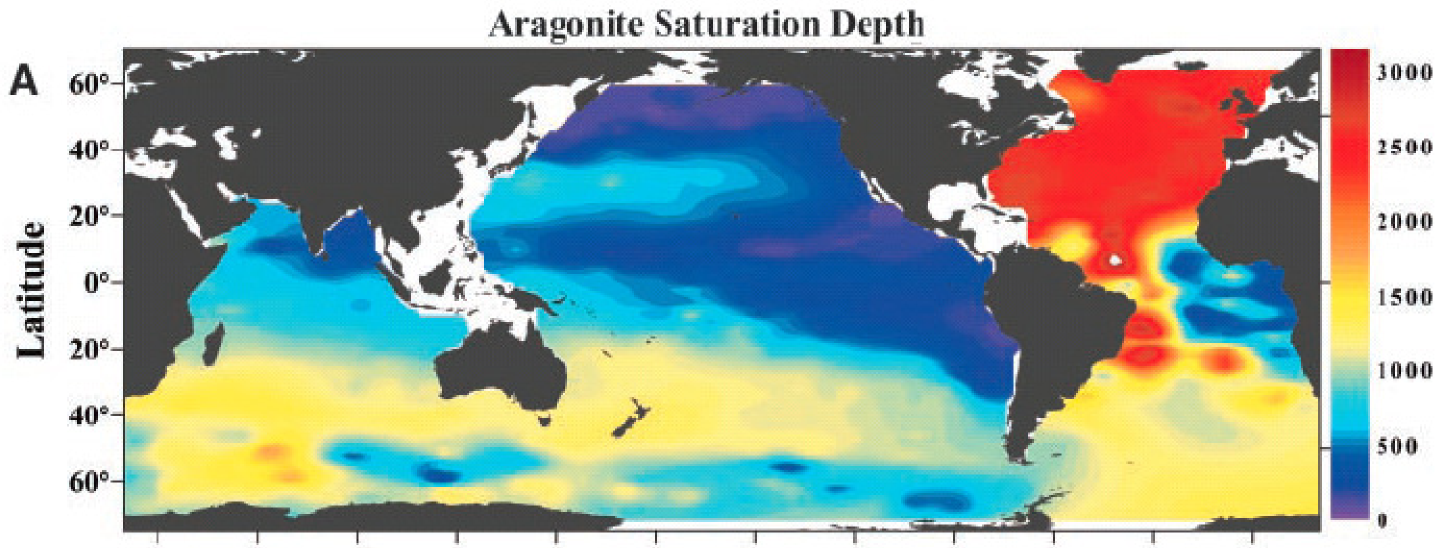
In order to assess this we should look at the response to the sea water bathing it now.

We can map the aragonite saturation depth in the world ocean with some accuracy from the JGOFS-WOCE survey

Impact of Anthropogenic CO_2 on the $CaCO_3$ System in the Oceans

Richard A. Feely,[1,*] Christopher L. Sabine,[1] Kitack Lee,[2]
Will Berelson,[3] Joanie Kleypas,[4] Victoria J. Fabry,[5]
Frank J. Millero[6]

The saturation depth in the vast region off the US west coast is less than 500m. The summit of Davidson seamount is far below this – it is already bathed in under-saturated water. Living corals overcome this. Dead ones dissolve rapidly.



Can we measure the effects of pH change on these systems?

Getting Permits? – A bizarre situation

The law locks up both man and woman
Who steals the goose from off the common
But turns the greater felon loose
Who steals the common from the goose

Society can freely dispose of 1 million tons CO_2 per hour in the ocean. A science team faces great difficulty in carrying out a few kg experiment! This makes no sense.

The London Convention of 1972 prohibits ocean disposal of anything not on a list – no one thought to include CO_2!

Decades of well-meaning ocean policy legislation prohibits "discharge" of various kinds, making small-scale perturbation experiments very difficult.

We need to change this.

Predicting the future? – Let's be careful; these are demanding and complex systems. What are we missing? – Where are the molecular links to adaptation? Where are the new technologies we will need to answer these questions?

Some special thanks – To DEFRA for supporting this meeting

- To ICES President Joe Horwood for establishing this WG

- To all of those here who will do the creative work