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Beyond Climate: The Emerging Science of a Low pH-High CO₂ Ocean

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Introduction

From its inception ICES has had a creative tension between the demands and linkages of fisheries and hydrography, and has superbly balanced those needs for more than a century of science. This has always seemed to me to be wise, and it is the extension of that theme towards the later part of the 21st century that is the subject of my lecture today. My message is simple; there are massive, and until very recently unrecognized, changes of geologic scale taking place in the ocean as we have entered the anthropocene era, and these may very well have profound impacts on ocean ecosystems world wide. I hope that unraveling these effects so that we do not go blindly into this brave new world will be a task for ICES scientists.

One hundred years ago Martin Knudsen and colleagues in a small laboratory in Denmark laid down the basis for the gravimetric measurement of ocean salinity (Knudsen, 1901; Forch, Knudsen and Sorensen, 1902). But if the equivalent sea water samples were to be measured today, even with the crude procedures of the time, a different result would be obtained. Ocean salinity has increased, not by evaporation of water but by the massive quantity of carbon dioxide added by mankind (Brewer, 1997); Knudsen could simply have weighed the difference, and chemistry is now impacting hydrography.

While the climate impacts of increasing atmospheric CO₂ levels have received great attention, the direct effects of the enormous CO₂ enrichment of the upper ocean have had little discussion. That is about to change, for ocean chemistry is being altered on a scale not seen for millions of years, and there are very basic questions on the impact on ecosystems and biogeochemical cycles to which we simply do not yet have answers.

Background

The role of the ocean in moderating the atmospheric CO₂ increase has been recognized for a very long time. Callendar (1938) noted the oceans role as “a giant regulator of carbon dioxide”, Revelle and Suess (1957) first explicitly calculated the partitioning of CO₂ released to the atmosphere between air and sea and estimated that ~40% of the gas would quickly be absorbed by the surface ocean, with the remainder building up in the atmosphere and changing climate. Oeschger et al. (1975) provided the first high-resolution ocean box-diffusion model designed to simulate this process with greater accuracy, and calibrated this model with radiocarbon data. With the initiation of the worldwide surveys of the GEOSECS program in 1972 the modern era of defining the CO₂ status of the worlds oceans began.

The scientific attacks described above basically treated the CO₂ transient as a “tracer” problem. That is the chemical complexity of CO₂ in all its forms in sea water, the relatively small size of the fossil fuel signal compared to the large natural abundance, and the difficulties of high accuracy measurement, all combined to make scientists wary of the direct recognition approach. Thus proxy measurements of the tracers radiocarbon, tritium, and Freons were all used to estimate ocean mixing and exchange rates, where the CO₂ signal was then inferred from these proxy measurements.

The ocean absorption of fossil fuel CO₂ is a function of sea water alkalinity. In the very simplest terms carbonic acid, formed by dissolution of CO₂ in water, reacts with calcium carbonate dissolved in a slightly alkaline ocean to form bicarbonate. The result is an elevation of ocean CO₂ levels and a decrease in pH. Yet so complex is the full accounting of this process that this message has often been blurred. The use of a confusing set of apparent thermodynamic constants, the existence of several pH scales,

the arcane distinctions between $p\text{CO}_2$ and $f\text{CO}_2$, the strictures on careful measurement, and the use of these systems in dynamic models have all deterred the non-specialist.

So strong has been the focus on carbon budgets and climate that fields such as deep-sea physiology have proceeded largely unaware that the basic chemistry of the ocean around them is changing.

Recognizing the fossil fuel CO_2 signal

Brewer (1978) first provided the procedure for directly extracting the fossil fuel CO_2 signal from the oceanic background, followed shortly afterwards by Chen and Millero (1979). The approach is to take measurements of the total CO_2 content and alkalinity of a water sample at depth, and ask how much they have been chemically altered since they were last exposed to the atmosphere. From the decrease in dissolved oxygen compared to equilibrium with the atmosphere, and the increase in nitrate, we can correct for CO_2 added from respiration and the regeneration of nutrients. From knowledge of the close correlation between salinity and alkalinity in surface waters we can correct for alkalinity (and CO_2) added by dissolution of calcium carbonate at depth. By subtracting these components from the observed signal the original CO_2 system properties of a parcel of water may be recovered. The algorithm, after reduction of the Redfield ratio constants, is simply:

$$\Delta\text{TCO}_2 = 0.8297\Delta\text{O}_2 + 0.5\Delta\text{TA}$$

The first published example of this is shown here from Brewer (1978).

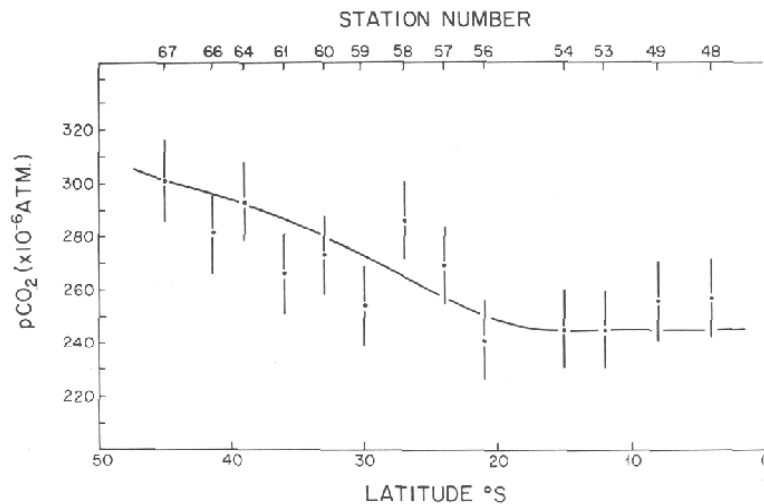


Fig. 2. The calculated initial $p\text{CO}_2$ of samples taken at the core of the salinity minimum of the Antarctic Intermediate Water in 1972.

Figure 1. A copy of Fig. 2 from Brewer (1978) showing the first attempt to recover the oceanic fossil fuel CO_2 signal by examining samples along the core of the Antarctic Intermediate water. The offsets from the true atmospheric pre-industrial signal represent both errors in the data set, and disequilibrium between air and sea at the time of water mass formation.

The publication of these papers caused concern for they broke the barrier of reliance on the proxy tracer approach, and there was a sense that errors in the Redfield coefficients used to apply the corrections could easily accumulate and invalidate the signal.

These concerns are no longer valid. Over the years forces have combined to transform the original signal so painstakingly uncovered into a massive and easily recognizable change in ocean chemistry. The analytical techniques used for measurement at sea were improved by at least a factor of 4. Standard solutions, patterned in many ways on the ICES Standard Sea Water model were produced. Corrections for any initial disequilibrium between air and sea were applied (Gruber et al., 1996). The JGOFS/WOCE program adopted a global ocean CO₂ survey in the late 1980s-early 1990s period that has provided a superb snapshot of an evolving chemical signal (Wallace, 2001). And the fossil fuel CO₂ signal grew to unprecedented size so that its impact could no longer be ignored.

The size of the oceanic fossil fuel signal today

With the formal series of assessments of climate by the Intergovernmental Panel on Climate Change (IPCC) came the need for more accurate estimates of the accumulated burden of fossil CO₂ now held by the ocean, and the ability to chart its future course. There are now many estimates of this, and they show a striking agreement. A detailed account is available in Field and Raupach (2004). Perhaps the most recent estimate, based upon the JGOFS/WOCE global survey carried out in the late 1980's to early 1990's, is that of Sabine et al. (2004) who conclude that the oceanic fossil fuel CO₂ signal accumulated from 1800 to 1994 is 118 ± 19 petagrams of carbon; this is 433 billion metric tons of CO₂, and the oceanic sink over this period has accounted for ~48% of the total fossil fuel released to the atmosphere during this period.

Ten years have gone by since the conclusion of the field observations summarized here. In 1994 the atmospheric CO₂ level was ~357 ppm, or 77 ppm above the pre-industrial level. In 2004 the atmospheric signal is ~380 ppm, or 100 ppm above pre-industrial; an ~ 30 % increase in 10 years. Put another way, the invasion rate of industrial CO₂ across the ocean surface is estimated as ~2 petagrams C/year (IPCC, 1995) or ~7 billion tons CO₂ per year. Thus in the decade since 1994 we have added an additional ~ 70 billion tons CO₂, and the accumulated ocean burden must therefore be about 500 billion tons at the time of giving this lecture. Since the atmospheric CO₂ level has risen in the last ten years, the oceanic invasion rate has risen also, and thus the oceanic invasion rate of fossil fuel CO₂ must now be close to 1 million tons CO₂ per hour.

Projecting the future

No one can predict the future with great certainty but there is an obligation to try. The IPCC reports contain a widely used set of climate forcing and emissions scenarios of which the most widely used for illustrative purposes is the IS92a "Business as Usual" scenario (Houghton et al., 1995). The term "Business as Usual" is a misnomer- the projections made assume for example that in 100 years renewable and nuclear technologies will provide more than 75% of all electric power, compared to 24% in 1990. That non-carbon technologies (including solar and wind) are assumed to grow to about twice the size of the entire global energy system in 1990 and that energy consumed per

unit of economic activity will decline to 1/3 of 1990 levels. While there are many other scenarios all scientists who have examined the problem facing society have recognized that unless there are truly enormous shifts in energy technologies the world will face unprecedented CO₂ levels within the next few decades (Hoffert et al., 2002).

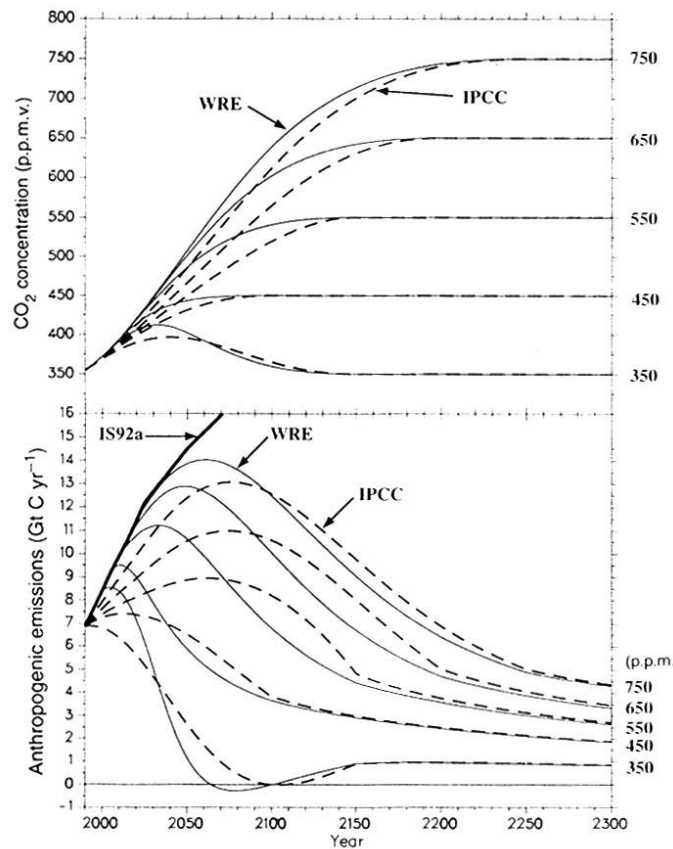


Fig. 2. A version of the IPCC IS92a emissions scenario (bold line, lower panel), together with pathways for atmospheric CO₂ stabilization as modeled by IPCC and by Wigley et al. (WRE). From Wigley et al. (1996). The difference between the IS92a scenario and the stabilization curves indicates the magnitude of the changes required to stabilize CO₂ levels.

A very large fraction of the available fossil fuels will be burned, and the CO₂ transferred to the ocean. The principal uncertainty is in the time scale, and the usually unspoken assumption behind plans for slowing fossil fuel CO₂ emissions to moderate climate change is to give more time for the ocean to absorb the excess CO₂. In short, all nations whether maritime or landlocked, count on ocean surface CO₂ disposal as a primary component of energy/climate policy. Continued ocean uptake is a critical component of the figure above.

The ocean impact of “Business as Usual”

While the climate impacts on the ocean caused by higher atmospheric CO₂ levels have received widespread attention, the direct chemical effects have received little attention until now. The first comment on the significant changes in ocean pH associated with IS92a was by Haugan and Drange (1996). Brewer (1997) provided the first detailed chemical analysis, and the changes in ocean CO₂ chemistry predicted are shown in the table below.

It is clear that by mid-century or shortly thereafter we could approach atmospheric CO₂ levels of ~600 ppm, and thus surface ocean chemistry changes of ΔpH ≅ 0.3. By the end of this century far larger changes are possible. Of critical concern is the change in carbonate ion [CO₃²⁻] concentration, essential for forming the shells of calcareous marine organisms and for coral reefs, which may decline by an astonishing 55%.

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

<u>Time</u>	<u>pCO₂</u>	<u>Total CO₂</u>	<u>pH</u>	<u>HCO₃⁻</u>	<u>CO₃²⁻</u>	<u>H₂CO₃</u>
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

Fig. 3. From Brewer, 1997. The table shows the calculated changes in ocean CO₂ system properties predicted under IS92a. By ~2060 surface ocean pH will have declined by ~0.3 pH units. By the end of the century it is possible that CO₃²⁻ ion will have declined by an astonishing 55%. It is very likely that these changes will occur.

Solving the “Climate Problem”?

The goal of the U.N. Framework Convention on Climate Change is to achieve “stabilization of green-house gas concentrations ... at a level that would prevent dangerous anthropogenic interference with the climate system.” Figure 2 above gives some pathways for achieving this. It requires enormous displacement of fossil fuel emissions to the atmosphere. For example, Brewer (2000) pointed out that this calls for displacement of 3.67 billion tons CO₂ per year by ~2025, and 14.7 billion tons by ~2050. These are prodigious quantities; recall that these numbers are equal to the entire world CO₂ output in 1932, and in 1967.

There are many ways proposed to achieve this, including nuclear, solar, wind, and biomass technologies. But the fossil fuel reserves are critical to any energy scenario and capture and disposal of the CO₂, rather than free release to the atmosphere, is a widely discussed option (Gale and Kaya, 2003), and is now the subject of a formal IPCC report. In such schemes the CO₂ stream is captured, for example by amine scrubbing, purified, compressed to liquid form and transported by pipeline to a disposal site. The process is still expensive and energy consuming with the costs being primarily associated with the capture and compression steps, common to all disposal sites. The best estimate today is that the economic, or energy, penalty associated with this process is 30-35%. It is not yet known how society will view this looming trade-off between energy costs and climate.

Disposing of CO₂ in the Ocean

Once CO₂ has been captured, say from a large-scale power plant, the question of where to dispose of it arises. Two options are available: underground in locations such as depleted oil and gas fields and deep saline aquifers, or in the deep ocean. Marchetti (1977) first proposed injecting captured CO₂ into the waters flowing over the Mediterranean sill into the mid-depth North Atlantic where it would be isolated from the atmosphere for centuries. The proposal aroused curiosity, but caused no great alarm. Since vast quantities of CO₂ are disposed of in the ocean anyway this may be seen as simply accelerating a “natural” process in which mankind first disposes of CO₂ in the atmosphere where it contributes to global warming, and then after a delay of a few years it is absorbed by the surface ocean. In short some 85% of the emitted CO₂ will end up in the ocean anyway, so why not accept this and proceed directly, thereby minimizing the climate threat?

This proposal was discussed and modeled for some twenty years without action. Plans were laid to carry out experiments, but were forestalled by a bizarre assortment of permitting and political issues (Haugan, 2003). Independently of this questions arose as to the stability of clathrate hydrates of methane on the ocean floor in the face of global warming. Both CO₂ and CH₄ will form a solid hydrate (Gas.6H₂O) by reaction with sea water at low temperature and high pressure, and a major report to the President of the United States (PCAST, 1997) recommended parallel investigations of the extraction of energy from deep-sea methane hydrates, and the permanent disposal of the CO₂ artifact of energy use as a hydrate on the ocean floor.

Novel experimental investigations of the formation and dissociation of methane hydrates in the ocean had already been carried out, and these techniques were quickly extended to CO₂ hydrates (Brewer et al., 1998). We now know both from empirical reasoning, and from experiment (Rehder et al., 2004) that CO₂ hydrate will dissolve quite rapidly in sea water since the aqueous phase is enormously under saturated with dissolved CO₂.

Modeling of the fate of CO₂ injected into deep ocean water has proceeded apace (Orr et al., 2003), and the results are now clear. The ocean retention time is strongly correlated with depth of injection, the local pH/CO₂ field is perturbed, and re-emergence of the CO₂ enriched water in the Antarctic upwelling region after some centuries of isolation from the atmosphere will result in some return of CO₂ from ocean to atmosphere, followed by re-absorption by the ocean. The expected result is “peak shaving” of the anticipated atmospheric CO₂ signal.

Carrying out ocean CO₂ experiments

The physical behavior of CO₂ in sea water is complex, and experimental advances were thus dependent on advances in technique. The first controlled CO₂ injection experiment (Brewer et al., 1998) relied upon helium pressure to expel liquid CO₂. This was not ideal due to the finite solubility of He in CO₂, and purely mechanical accumulator containment and delivery systems were soon developed (Brewer et al., 1999). CO₂ exists in the liquid state below depths of ~400m for typical oceanic conditions. It is a highly compressible fluid, and thus its density increases with depth, reaching neutral buoyancy at about 2,750m depth, and forming a sinking plume at depths below 3,000m. It will react with sea water to form a solid hydrate at depths typically below about 350m, and it is some 10x more soluble in sea water than any other atmospheric gas. Once hydrated it partitions into the well known ionic species HCO₃⁻ and CO₃⁼ that characterize the dissolved ocean CO₂ system and indicate its pH.

Models show that the time of ocean retention of injected CO₂ is strongly correlated with depth, and thus there is keen interest in deep (>3,000m) injection techniques. An image from the first such experiment is shown in Fig. 4.



Figure 4. A 4L beaker filled with liquid CO₂ at a depth of 3,600m is inspected by a Pacific Grenadier fish. The CO₂ has reacted with sea water to form a hydrate, and the volume expansion has caused spill over of the liquid. From Brewer et al. (1999).

The fortuitous observation above of marine animals close by a CO₂ release quickly led to the realization that biological impact studies were possible, and the first such field work has now been elegantly done (Tamburri et al., 2000; Barry et al., 2004).

Environmental Concern?

The bold and successful execution of the experiments above crystallized concern over the possible impacts of ocean CO₂ enrichment (Seibel and Walsh, 2001, 2003). Yet such

concerns may be misplaced. The problem addressed is the claim that many deep-sea animals are highly sensitive to ocean $p\text{CO}_2$ levels, which may “lead to large cellular $p\text{CO}_2$ and pH changes. Oxygen transport proteins of deep-sea animals are also highly sensitive to changes in pH” (Seibel and Walsh, 2003).

Yet if such concerns are true the world has a far, far larger and very real problem. In practice there are no concrete plans for such intervention by governments on a large scale. And even if such a scheme were carried out in the far future, the ability of mankind to approach by direct engineering even a tiny fraction of the amount of CO_2 invading the ocean today is limiting. Model calculations show that a hypothetical release for 100 years at a rate of 0.37 billion tons CO_2 per year at each of 4 points would result in an ocean pH reduction of >0.3 pH units in less than 0.01% of total ocean volume (Wickett et al., 2004).

In sharp contrast to such hypothetical events there are near certainties facing the entire ocean already. Figure 3 above lists the trend in ocean pH to be expected with time. Caldeira and Wickett (2003) have extended this work. In Figure 5 is shown the projected change in whole ocean pH simply from atmospheric invasion under IS92a, followed by extension of that scenario until all known fossil fuels are burned. It is very possible that we will proceed along this path.

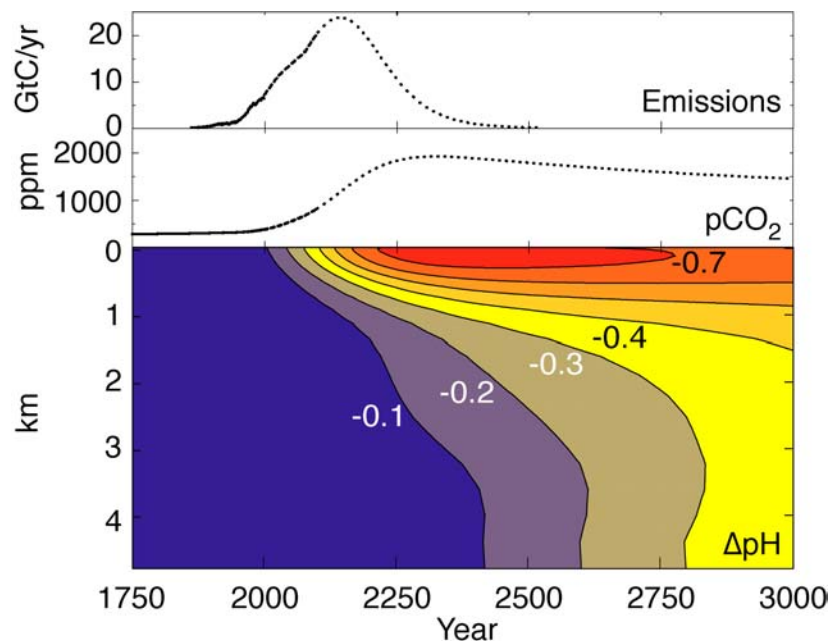


Figure 5. The projected change in ocean pH from pre-industrial to the year 3000 from burning of all fossil fuels with emission of the CO_2 to the atmosphere. A change of ~ 0.3 is expected in the second half of this century. Stabilization of atmospheric CO_2 at 550 ppm implies eventual ocean storage of about 6,200 billion tons of CO_2 . From Caldeira and Wickett (2003).

Effects of changes in ocean pH on marine ecosystems

With the latent realization that changes of such scale are already in progress, and very likely to continue, there has been a recent upsurge of biological concern. Riebesell et al.

(2000) have investigated the reduced calcification of marine plankton in response to increased atmospheric CO₂. They reported reduced calcite production at increased CO₂ concentrations of the common oceanic species *Emiliana huxleyi* and *Gephyrocapsa oceanica*. Significant impacts on coral reefs have been predicted by Kleypas et al. (1999). Experiments in controlled tanks (Langdon et al., 2000) have led to predictions of 40% decrease of calcification in coral reefs under CO₂ doubling conditions.

Portner et al. (2004) have provided a detailed and scholarly account of the biological impact of elevated ocean CO₂ concentrations on marine animals. They report that elevated CO₂ levels “are expected to affect long-term growth and reproduction, and thus may be harmful at population and species levels.” They found maximal sensitivity in ommastrephid squid. In support of this broad concern Shirayama and colleagues (Kurihara et al., 2004) report significant sub-lethal effects of elevated CO₂ levels on planktonic copepods and sea urchins, in which basic reproduction was affected by pH/CO₂ changes well within the range reported in Fig. 5.

The next generation of ocean experiments?

The papers above, and many others, are based upon well-founded concerns. They open the window to very broad questions over the future functioning of marine ecosystems worldwide. How might these concerns be addressed? There will no doubt be a vigorous experimental attack on marine organisms of many kinds to investigate their response to elevated CO₂ levels. But I approach this problem from the perspective of a marine chemist, and ocean chemists are often chided by their biological colleagues for not taking an ecosystem approach. Let me accept the challenge. What might such an approach look like?

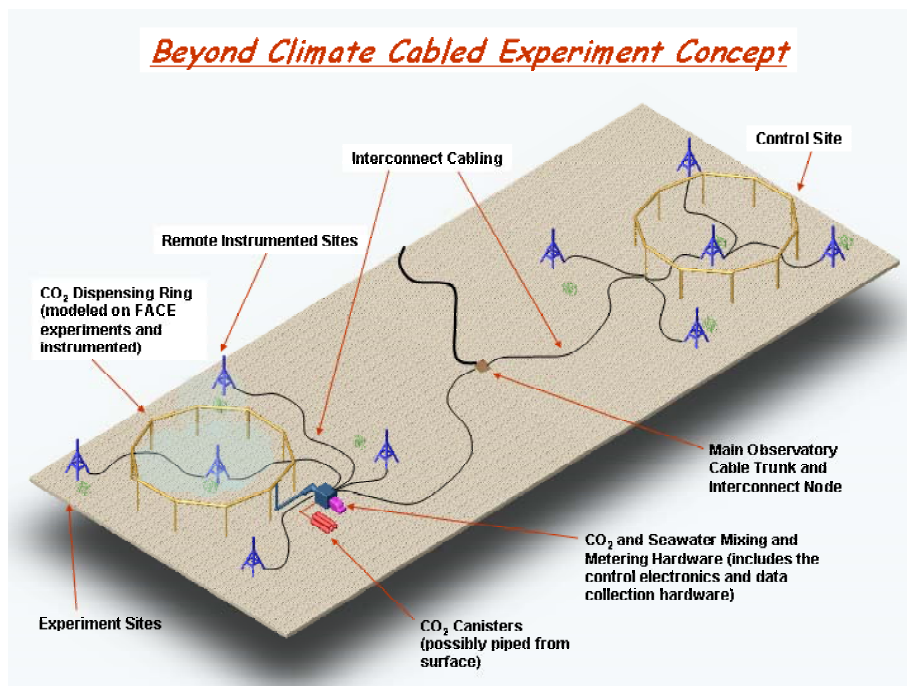
We have excellent analogs in large-scale CO₂ enrichment experiments now routinely carried out on land (DeLucia et al., 1999; Shaw et al. 2002). One example of very large scale is shown in Figure 6.



Figure 6. A FACE (Free Air CO₂ Enrichment) experiment in Wisconsin. The tall towers leak CO₂ into the local air at rates controlled so as to bathe the local vegetation in CO₂ levels that simulate the predicted conditions of the later part of this century. Release rates are compensated for wind speed and direction. Quite large CO₂ releases are required – one FACE site releases about 1,000 tons CO₂ per year.

What is the possibility of creating an equivalent set of Free Ocean CO₂ Enrichment (FOCE) experiments? The challenge is daunting. The atmosphere has essentially no active CO₂ chemistry – the released gas simply mixes. The ocean has a complex chemistry, with significant kinetic affects. In particular the hydration rate of the CO₂ molecule is slow (Johnson, 1982), and at low temperatures it may take many minutes for equilibrium to be achieved. In this case the admixed CO₂ could be advected beyond the desired control volume before equilibrium with the local ocean water is reached. Nakayama et al. (2004) have recently shown that there is a significant enhancement of the hydration reaction rate at pressure, driven by the large negative volume change of the hydration reaction. Thus deep, cold experiments may very well be possible.

A sketch of one possible system is shown in Figure 7 (W. Kirkwood, pers. comm.). It portrays the concept of a cable for experimental control, and a small-bore pipe for supplying CO₂, or CO₂ enriched sea water, to a set of controlled volumes on the ocean floor where experiments are located. The size, duration, selection of experimental processes, and biogeochemical phenomena etc. are all to be determined. Successful execution of this would be a considerable challenge.



Conclusions

I have attempted to present, in somewhat narrative form, an account of the progress in ocean CO₂ biogeochemistry over the last decade or so. What is clear is that while there may be some uncertainty over the course of the climate impacts of elevated CO₂ levels, there is no such uncertainty over the projected chemical changes. We will have an ocean of lower pH than this planet has seen for very long stretches of geological time; and we are at a very early stage of recognizing the scale of this, and in acquiring sure knowledge of the impacts on ocean ecosystems worldwide (Cicerone et al., 2004).

In spite of this lack of knowledge there are many strong opinions – those who “feel everything is OK”, and those who see serious problems looming. The job of scientists must be to provide some sure answers as we go forward.

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