Roger Revelle Commemorative Lecture

Contemplating Action:
Storing Carbon Dioxide in the Ocean

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Introduction by D. James Baker

I appreciate the opportunity to say a few words about Roger Revelle and to introduce Peter Brewer. The title of my short introduction today is "Flying Beans, Jack and the Beanstalk, Botanical Whales, and Coral Reefs." And it is all completely relevant to the subject at hand. But let me begin by saying that I knew and worked with Roger and I know and am a colleague of Peter. Their work in that most integrating of fields, ocean chemistry, spans contemporary earth science, and it is fitting to honor both during this National Chemistry Week. And also to have this talk here at the National Academy of Sciences. Roger was a force in the predecessor committee of today's Ocean Studies Board, and Peter has been a two term member and a major contributor.

Roger Revelle's accomplishments are legendary in earth sciences, and he had a huge effect on application of science to practical problems, from energy policy to feeding the world's growing population. I've had the privilege of seeing oceanography from the academic world and the government policy world, and I appreciate Roger's influence and breadth more because of that dual view. Peter's talk today illustrates his considerable and ongoing influence on both the science and policy world.

Roger Revelle published his first paper in 1934, more than 65 years ago, on the subject of calcium carbonate in sea water a beginning to his long interests in carbon in the sea and in the atmosphere. This first work led to the wellknown developments of measurement and impacts of increasing carbon dioxide in the atmosphere and all the discussions of global warming.

Today's talk is focused on the practical application of ocean science to a major problem. Therefore I would like to speak to the other side of Roger Revelle—his interest in the practical aspects of science applied to the developing world. In 1978, he published an important, but much lesser known work, on underexploited tropical plants in the Annual Report of the National Research Council: "Flying Beans, Jack and the Beanstalk, and Botanical Whales."

This paper was a far cry from calcium carbonate, but equally important to the world. Flying beans produce edible green pods in two months and beans after four months; yields are as large as soybeans, and the crop could rival soybeans. Rapidly growing trees, such as the *Leucaena*, can grow to a height of nine meters in two years, twenty meters in six to eight years. Annual growths can be twelve to fifty tons per hectare: as close as a living plant can come to the beanstalk that Jack climbed. Botanical whales refers to jojoba: a slate green twiggy stunted shrub. Half the weight of the nut is a yellowish, odorless polyunsaturated liquid wax, much like sperm oil. At the time Revelle wrote this, 20,000 sperm whales were being killed per year for their oil. Commercial whaling has stopped, but the search for oil substitutes continues.

Roger served two institutions: Scripps Institution of Oceanography, and Harvard University, and he spent two years in Washington advising the Secretary of the Interior. He kept these dual, parallel and connected tracks active until he died, exemplifying the true renaissance man.

Well, our speaker was not publishing papers in 1934. But we can ask what was he doing in 1978,

while Roger Revelle was talking about botanical marvels? Peter Brewer was in fact demonstrating the breadth of his interests with three published papers that year: with Mary Scranton on "Consumption of dissolved methane in the deep ocean," with Mike Bacon and Derek Spencer on "Lead 210 and Polonium 210 as marine geochemical tracers: review and discussion of some recent results from the Labrador Sea," and by himself on "Direct Observation of the oceanic CO_2 increase." Peter's accomplishments are demonstrated by that year of papers, which show how he goes about extracting the oceanic signals of global change, and developing novel techniques for measurement.

Peter Brewer also has served two institutions: Woods Hole Oceanographic Institution and the Monterey Bay Aquarium Research Institute. And, like Roger, he spent two years in Washington. He has shown a deep interest in ship design and institution building, and has been successful at both. And finally, like Roger, Peter has also shown an interest in the practical solution of global problems. Just as Roger Revelle looked at new agricultural practices and explored the environmental consequences of growing new kinds of plants, Peter Brewer is looking at new ways to deal with CO_2 and the environmental consequences.

As a consequence of human activity, atmospheric carbon dioxide is steadily growing. Can this increase be stored in the ocean? This brings me finally to the topic of coral reefs. I just returned from the U.S. Virgin Islands where we had the third meeting of the U.S. Task Force on Coral Reefs, appointed by the President as a result of last year's National Ocean Conference. At the meeting, carbon sequestration was noted as a critical topic for the world. The question was raised what will happen to the coral reefs if CO_2 is pumped into the ocean for storage? I thought: this is a good question for Peter Brewer, and is just one of the many issues that relate to today's subject.

Active intervention in a natural system for the good of mankind is the overarching theme. In his book *The New World of the Ocean*, Daniel Behrman says that "More than any single figure, Roger Revelle is responsible for the introduction of oceanography into public affairs." Peter Brewer continues that theme.

It is my pleasure to introduce a great ocean chemist, Dr. Peter Brewer.

– **Introduction for First Annual Roger Revelle Lecture by Dr. Peter Brewer November 9, 1999 National Academy of Sciences**

D. James Baker • Under Secretary of Commerce for Oceans and Atmosphere

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Introduction

It is a great pleasure to give this, the first Revelle Commemorative Lecture, for I had the privilege both to know Roger over the last decade of his career, and to work on problems in which he was keenly interested. Roger of course did not personally establish that carbon dioxide was increasing in the atmosphere; that was recognized much earlier in the century (1). But his passion for this problem, and his leadership (2), his uncovering of what we now call the "Revelle Factor" for carbon dioxide buffering of the ocean, and his hiring of Dave Keeling at Scripps during the IGY years to make the first wonderful series of atmospheric measurements, are surely the basis for the world wide interest today. Roger also wrote one of the first papers on gas hydrates in the oceans, and introduced me to the subject. These amazing compounds will make their appearance in the lecture I give today.

The end of the experiment? It is now 42 years since Revelle and Suess wrote their seminal paper (3) with the now legendary phrase "human beings are now carrying out a large scale geophysical experiment" that so captured the imagination of large numbers of scientists.

But all experiments are expected to have a result, and it may be supposed that we have reached one today. The temperature signal is only just emerging from the noise, and its trajectory is still uncertain. But within the last few years an enormous international debate has taken place, with the conclusion by the Intergovernmental Panel on Climate Change (IPCC) that "the balance of evidence suggests a discernible human influence on climate" (4). And we have the announcement of a goal by the UN Framework Convention on Climate Change (UNFCCC) to achieve "stabilization of greenhouse gas concentrations ... at a level that would prevent dangerous anthropogenic interference with the climate system." One recent example (5) of the present rapid change in northern hemisphere temperatures is shown in Figure 1. The question now shifts to what we are going to do about it. And the role that active intervention, through carbon sequestration in the ocean, may play in achieving this goal is the focus of this lecture. This was recently recommended by the President's Council of Advisors on Science and Technology (PCAST), and must be taken as a serious question. But

is this even possible? What is the underlying science? And where do we go from here?

It is of course deliberately provocative to suggest this. For four decades the scientific response has been to measure, to model, to uncover quite beautifully the powerful fluctuations of greenhouse gases and climate in the Earth's past, and to issue warnings both sober and dire about the future. This work will continue, and we may expect the continued evolution of elegant models, and the establishment of monitoring networks and stations of increasing sophistication as the march of our industrial society is measured. Surely determining what "dangerous anthropogenic interference" actually is, as a risk concept in the intrinsically turbulent coupled ocean-atmosphere system, will be profoundly difficult.

But if all we do as scientists is to measure, model, and warn, then our value to society may be limited. What additional role may we play? And can we provide solutions as well as define the problems?
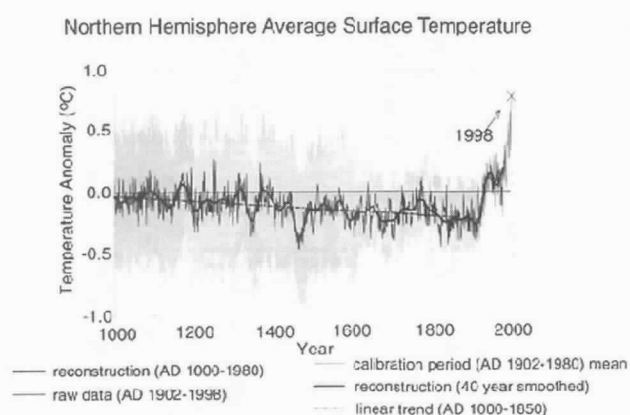

Figure 1. Reconstruction of Northern Hemisphere temperature anomaly trends from 1000 A.D. to present. From Mann et al. (5).

The size and timing of the problem. It would be hard to argue against a primary strategy of reducing emissions, but it may not be easy or even possible on the scale required. Few people truly understand the scale of the transition that is being debated today. The problem is to diverge from our present trend of rapidly rising temperatures and greenhouse gas concentrations while maintaining a technologically advanced society and maintaining worldwide economic growth. Perhaps the most widely cited analysis is that given by Wigley et al. (6), who took the illustrative pathways of the IPCC (4) for stabilizing atmospheric CO_2 levels at 350, 450, 550, 650, and 750 p.p.m.v. over the next few hundred years. They re-analyzed these trajectories incorporating explicit economic considerations for selecting a concentration path. The conclusions are generally recognized as being robust, and were recently adopted by the U.S. Dept. of Energy (7) as a useful target. Figure 2 is taken from this report. It shows one such calculation of the departure required from the IPCC global "Business as

Usual" scenario if atmospheric stabilization at about 550 p.p.m.v. (about twice the pre-industrial level) is to be achieved. The numbers are strikingly large; about 1 GtC/year by 2025, and about 4 GtC/year by 2050 are required by the efforts of all nations if the 550 p.p.m.v. target is to be adopted.

These are prodigious quantities. To put these numbers in perspective recall that 1 GtC/year was approximately the entire world carbon dioxide output in about 1932, and 4 GtC/year the output of the world in about 1967. It may be that global economic growth does not lead to such high emissions, or that the climate effects may be smaller or more benign than anticipated. Early workers (1) suggested that the effect "is likely to prove beneficial to mankind in several ways" and a minority holds this view today. Or some new and unanticipated energy technology may arise. Nonetheless it now appears to be prudent to be well prepared to deal with the problem.
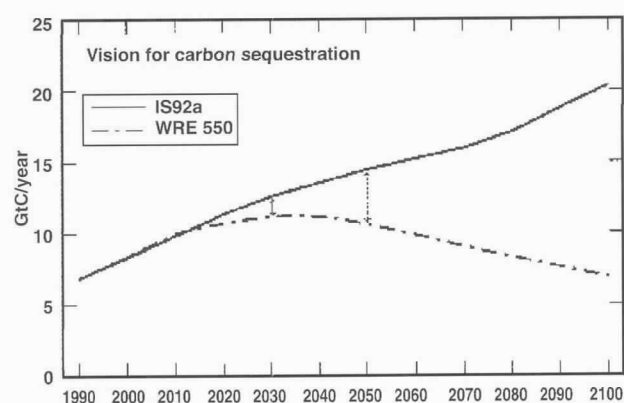

Figure 2. One representation of the reduction in CO_2 that would be necessary to reach atmospheric stabilization by comparing the IPCC IS92A ("Business as Usual") scenario with calculations (WRE 550, ref. 6) of emissions trajectories designed to stabilize atmospheric CO_2 levels at 550 p.p.m.v. (about twice the pre-industrial level). From ref. (7).

The options. The policy options have been exhaustively debated, and need not be repeated here. For instance the 1992 report (8) by this National Academy of Sciences is exemplary. In brief we may conserve or enhance efficiency, and we may substitute alternate energy sources such as nuclear and solar power. We may shift towards other fossil fuel mixes such as the dominant use of methane over higher hydrocarbons, and we may consider carbon sequestration through the enhancement of sinks or through deliberate disposal strategies. This topic of "sinks" is now much debated, and it has a contentious place in international deliberations.

The UNFCCC "Kyoto Protocol" adopted in 1997 gave special consideration to carbon sinks, but chose a narrow wording. In this document "sinks" were limited to "direct human-induced land-use change and forestry activities, limited to afforestation, reforestation and deforestation since 1990". In this narrow definition CO_2

disposal would not technically be a "sink," but could be recognized as "emissions foregone". The ocean was not mentioned here, but as we shall see it occupies a crucial place in the carbon cycle.

In the enthusiasm to take advantage of the attention given to carbon sinks on land several adventurous claims were made. For instance Fan et al. (9) claimed that the forests in North America took up 1.4 ± 0.4 GtC/year, as opposed to only 0.1 GtC/year by the forests of Eurasia. Such a large sink is politically attractive to the United States, and would offset completely the continental fossil fuel emissions. But it does not appear to be realistic. Informed comments on this work by others (10, 11) place the true U.S. carbon sink far lower, at perhaps one tenth of this amount. Moreover it well recognized that carbon storage on land has a strong temporal, rather than permanent, component. Once a forest matures, then carbon is released back to the atmosphere by decomposition and respiration.

In general we may believe that no simple answer or magic bullet exists, and that a mix of all options will have to be considered simultaneously if the goal of avoiding "dangerous anthropogenic interference" is to be achieved, whatever that level may be.

Uptake by the Ocean. The natural uptake of carbon dioxide from the atmosphere by the ocean occurs on an enormous scale, and the ocean offers the world's most powerful long-term buffer against the rise of both temperature and CO2. Most of the carbon, about 90%, released from the burning of fossil fuels will eventually end up in the ocean. But this will take more than a thousand years to reach equilibrium if the buffering capacity of the carbonate sediments is properly accounted for. It is the relatively slow rate of the uptake process that permits the atmospheric build up we see today. Debate over the true amount taken up annually by the ocean is still a research issue; it has varied from the early estimates by Revelle and Suess (3), to the IPCC estimate (4) today of about 2.0 ± 0.8 GtC/year. The chemical capacity of the ocean for CO_2 uptake is enormous, but the rate at which this capacity can be brought into play is slow. Note that this natural "sink" is viewed as a chemical commons, and no nation can claim its share of credit for CO_2 taken up naturally by the ocean within it's territorial waters.

In contrast to a significant fraction of the uptake by biota on land, the gas invasion into the ocean is permanent. It results from the mixing of the ocean exposing sea water annually to the air, and gas exchange across the sea surface driven by winds and chemically forced by the increasing levels of CO_2 in the atmosphere. The rate is constrained not only by mixing, but by the chemical resistance imposed by Revelle's buffer factor so that the rate of gas exchange for CO_2 is some ten times slower than for a "normal" atmospheric gas such as O_2 or N_2. In order to affect this number we would have to find some way to increase the rate of ocean mixing, or change the buffer factor, on an enormous scale. This is not realistic.

However we are not powerless, and within the last few years two powerful new approaches to ocean carbon sequestration have emerged, direct CO_2 disposal and iron fertilization of phytoplankton growth, which have been explored in a daring series of highly original experiments.

Direct disposal is of course not limited to the ocean. CO_2 injection into oil reservoirs for enhanced recovery has long been undertaken, and an innovative Norwegian project at the Sleipner T Platform in the North Sea now injects recovered CO_2 into a formation below the sea bed specifically for the purposes of CO_2 mitigation. Direct injection into saline land aquifers has also been considered as a mitigation strategy.

Ocean CO₂ disposal

Direct ocean disposal of CO_2 was first suggested by Marchetti in 1977 (12). He considered capturing CO_2 from the combustion process and directly injecting it deep in the ocean. He suggested that injection into the deep dense waters of the Mediterranean outflow would carry the CO_2 burden into the deep Atlantic circulation, removing it from contact with the atmosphere for centuries. The time scale of the ocean thermohaline circulation was determined in the 1970s by the classic ^{14}C measurements of the GEOSECS program. In brief at present the deep waters of the world ocean are replaced on average every 500 years. The mean replacement time of the Pacific, Indian, and Atlantic Ocean deep waters are approximately 510, 250, and 275 years (15). Thus material placed in the deep sea may be sequestered for very long periods. Once the abyssal flow of the ocean has progressed sufficiently that this deep water is once again brought into contact with the atmosphere, far from itís starting point, the Revelle factor that was so important in slowing the invasion of CO_2 now works in our favor. Only a small fraction of the disposed gas will return to the atmosphere.

The attractiveness of this idea lies in its relative permanence and quantifiability; the problem lies in the cost, the significant energy penalty associated with capture, and the uncertainty over some fundamental scientific issues which are now rapidly being explored. There are many capable reviews of this problem (13), but only laboratory experimental work has been done until now.

First, an important note on the units used. For reasons of accepted convention the descriptions of the global carbon system are given as mass of carbon (C) alone. But we can not dispose of carbon alone, only CO_2 itself, and those oxygen molecules are heavy. 1 GtC = 3.66 billion metric tons of CO_2. The surface ocean today sequesters more than 7 billion metric tons of CO_2 per year.

Let us look at the big picture, and the truly vast capacity of the ocean. The volume of sea water is about 1.37×10^{21} liters, and the ocean waters contain about 40,000 GtC. The recoverable fossil fuel reserves are about 5,000 to 10,000 GtC, and if about 1,300 GtC were disposed of in the ocean it would on average lower the

pH only by about 0.3 units (7). The change in surface sea water pH resulting from gas invasion today is already 0.1 units (14), and this invasion of billions of tons of CO_2 is occurring in the upper ocean with it's abundant life, and coral reefs.

The details of injection at depth are more complex. The buffer capacity of the ocean involves not only the dissolved carbonate, but also the $CaCO_3$ as calcite and aragonite in marine sediments. The physical chemistry of the CO_2 molecule is such that at high pressure and low temperature it forms a clathrate hydrate, wrapping itself in a cage of water to form a solid compound, much like ice, that profoundly changes itís behavior. And the effects on marine life of CO_2 disposal, both acute and chronic, must be carefully weighed. If we are to consider large-scale disposal options by the year 2020 then it is important that we make early and significant scientific progress in understanding and observing these processes. These experiments have now begun (16), and the results are fascinating.
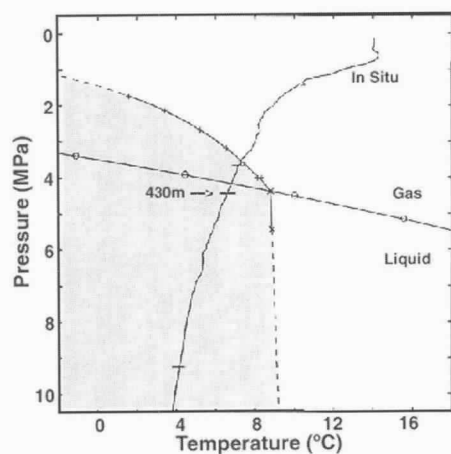
Figure 3. Phase diagram showing the P-T boundary below which (shaded area in diagram) CO_2 injected into sea water forms a solid hydrate. A typical sea water temperature/pressure profile from the ocean off northern California is overlaid. From Brewer et al. ref. (16).

CO_2 and Hydrates. Carbon dioxide readily forms a Structure I hydrate [$CO_2 \cdot 6H_2O$] when injected into cold deep sea water. The phase diagram giving the P-T boundary where this occurs is shown in Figure 3.

In fact the boundary is not so deep, and below about 350 m depth we may expect the transformation from a gas or liquid to a solid to occur. But so strange are the properties of this substance, and so difficult has it been to work with except for laboratory pressure vessel studies, that quite imaginative pictures of the anticipated oceanic behavior have resulted. An easily accessible review was recently given by Hanisch (17), and a sketch of various disposal modes (Figure 4) was presented.

We have carried out a series of ocean experiments to test such ideas by simply using modern remotely operated vehicle (ROV) technology to carry down the gas and perform a set of measurements on small quantities

of the released material.

Intermediate depth injection. Our first experiments (18) were carried out at about 910 m depth, and were designed both to perfect technique and to test ideas of the creation of a sinking mass of CO_2 from the density of the hydrate skin. While at these depths liquid CO_2 itself is less dense than sea water, the hydrate solid is more dense. And it has been widely suggested that the hydrate film may grow sufficiently thick that a bubble of liquid CO_2 will gain mass by progressive reaction with sea water and then sink into the abyss under itís own weight. Such behavior would be a great advantage to efficient disposal.
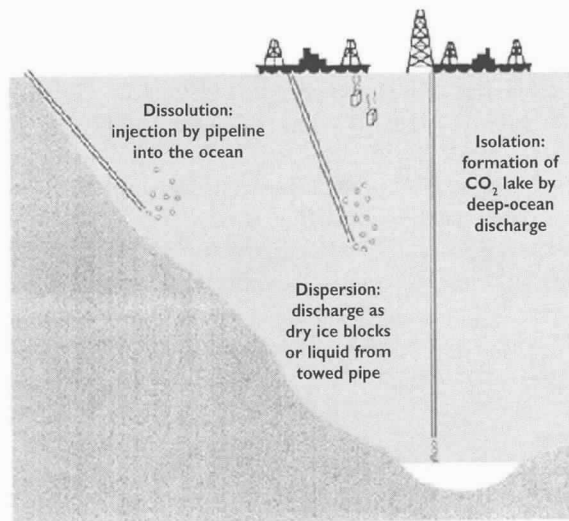
Figure 4. Sketch of various ocean CO_2 disposal options. Note the change in direction of the material from rising at intermediate depths, to sinking at great depth. This is caused by the much greater compressibility of liquid CO_2 than sea water. The neutrally buoyant point will be reached at about 2600m depth, depending on local conditions. Below that depth CO_2 release will sink to the ocean floor. From Hanisch (17).

Unfortunately, in spite of ingenious efforts, such sinking behavior has not yet been achieved and our observations show that CO_2 injected into the ocean at intermediate depths rises back towards the upper layers, undoing much the work spent. Very recent results suggest that both the growth rate of the hydrate skin, and the dissolution rate, are so slow that little mass transfer to the ocean occurs until the material rises close to the hydrate phase boundary shown in Figure 3. It may be that technical ingenuity can yet overcome this problem, but so far this has not been achieved.

The net result of transfer of large quantities of CO_2 which rise to about 300m depth is that the circulation of the upper ocean will quite rapidly expose these waters to the atmosphere, with sufficiently high local concentrations that some significant loss will occur. Elegant tests of the "ventilation age" of upper ocean water masses have been devised using chemical tracers such as the C.F.C.s and the ^3H-^3He pair (19). At these shallow depths sequestration time scales before atmospheric exposure of only a few years may be expected.

Deep-water injection. Since nature shows some resistance to our efforts at intermediate depths let us now look deeper. Note that in Figure 4 a curious reversal of properties is implied. While the droplets of CO_2 are sketched as rising at intermediate depths, they sink in deep water. This arises from both from the extraordinary incompressibility of water (fundamentally from hydrogen bonding), and the quite high compressibility of liquid CO_2. As we go to great depths the density ratio of these fluids reverses. We may now use this to advantage, and consider the fate of a gravitationally stable injection.

We have carried out such an experiment (16), and the results are surprising. The apparatus is quite simple, consisting of a steel accumulator and piston (much like a giant syringe) that was filled with about 9 liters of liquid CO_2. The vapor pressure of liquid CO_2 at room temperature is about 750 p.s.i. and so some reasonable care is required for this procedure. The assembly was secured within the frame of the MBARI ROV *Tiburon* and the various valves and actuators required for operation were connected to the vehicle hydraulic system. Calculations on the equations of state of both sea water and CO_2 showed that for the northern California site chosen for the experiment the neutrally buoyant point would be at about 2650m depth. The vehicle was thus flown well below this depth, to about 3627m, and set on the sea floor. Three experiments were carried out of almost Franklinesque simplicity; CO_2 was dispensed into a 4 liter laboratory beaker placed on the sea floor (providing only CO_2/sea water contact), then into a simple tube pressed into the sediment, and finally free release into a small depression on the sea floor.

Much had been written about the possible outcome of such an experiment, with suggestions of formation of an ice-like floating skin, of strong chemical reactions with the underlying sediments, of the problems with brine rejection and CO_2 rich pore waters, and so on. But the experiment had not been done.

The video imagery of the processes that followed are compelling (see http://www.mbari.org/ghgases/deep/release.htm for brief excerpts) and these have important consequences for effective disposal strategies. In only an hour or so we observed that the volume of liquid dispensed into the two containers was greatly increasing, and that the material dispensed onto the sea floor was swelling or elevating. It became clear that the experiment could not be contained, and soon a series of overflow events occurred, spilling CO_2 expelled from the containers onto the ocean floor. We were witnessing for the first time the fluid dynamics of an intense and rapid chemical reaction, with strong motions being generated. The overflow was an Archimedean displacement event, being driven by the incorporation of large volumes of water as a hydrate was formed. This then sank as a dense solid to the bottom of the containers, pushing remaining fluid out the top. Within hours our liquid was converted to a block of ice-like hydrate, imaged standing on the sea floor.

This has several important advantages for the sequestration problem. The hydrate itself will dissolve only very slowly (the temperature and pressure conditions for stability are far exceeded, but the ocean is undersaturated with CO_2) thus increasing the sequestration time scale. Slow release of CO_2 from a hydrate mass would minimize local concentration effects. Several animals swam by within a very few centimeters of the experiment, including a large fish (Fig. 5) and a sea cucumber, showing no apparent avoidance reaction and thus it is quite possible that biological impacts would be small.

Figure 5. A large Pacific Grenadier fish (Coryphaenoides acrolepsis) inspects a blob of liquid CO_2 on the ocean floor at a depth of 3627m. The existence of a thin transparent skin of the hydrate [$CO_2 \cdot 6H_2O$] forms a very strong barrier to CO_2 escape, and the animal apparently does not sense any chemical gradient.

There are many things we do not know here, including the lifetime of the hydrate, the effect on local sediments, and the long-term biological consequences. But since a window into experimental technique has been opened all these things are possible and can be rapidly explored.

Avoiding the hydrate? True shallow injection of CO_2, just above the point at which it will form a hydrate, has been considered (20), and in this case the solubility of CO_2 is so large that it in effect doubles the salinity of sea water and forms a dense brine that will sink. However the protection to marine life offered by the hydrate skin is no longer present, and observations show that close contact with this fluid would be harmful.

The carbonate sediments. The ultimate fate of fossil fuel CO_2 taken up by the ocean is to react with carbonate sediments. The invasion of CO_2 lowers the pH of sea water, but does not change the net ionic balance. This is eventually accomplished by the attack of this more acidic water on the calcium carbonate contained in marine sediments at depth. This increases the alkalinity of sea water and restores its buffer capacity. Surface sea water is supersaturated with respect to the biogenic carbonate minerals calcite and aragonite, but the cold deep

more acidic waters do dissolve these minerals, deposited on the sea floor by the rain of particles from above. This system is in dynamic balance, the rain of new material balancing on average the rate of dissolution. We know that these deep carbonate boundaries fluctuate in response to climate changes, and we can predict that the fossil fuel CO_2 burden being experienced by the ocean today will drive the dissolution boundary to shallower depths. This problem has complex dynamics (21) which have been elegantly examined and modeled by ocean scientists.

In brief the rate of ocean circulation is sufficiently slow that it will be many hundreds of years before humankind gains the benefits of the restored alkalinity from sedimentary carbonate dissolution forced by the downward mixing of waters labeled by the invasion of fossil fuel CO_2 from the atmosphere. However direct deep injection of fossil fuel CO_2 circumvents the slow penetration of deep waters, and CO_2 slowly leaking from a deep hydrate mass will encounter the restorative buffering of carbonates well before it is ever returned to the surface layers.

Evaluation. Both the energy and dollar costs of this procedure are dominated by the cost of capture of CO_2 from the combustion gas stream. This step is essential for any form of sequestration, be it in saline aquifers, in geologic structures, or in the deep sea. The transportation and injection costs may be about 15-20% of the total.

From the very few experiments carried out so far it appears that deep injection of CO_2, simply by using a longer pipe, offers powerful advantages over shallower injection although much remains to be done. The benefits of reduced environmental impact, long sequestration times, the prospect of very slow release rates, and the transfer of CO_2 close to the carbonate dissolution boundary are all very positive factors. It may well be possible to greatly enhance the lifetime of the hydrate mass, thus reducing or effectively eliminating the CO_2 transfer to overlying bottom waters.

Ocean Fertilization

Oceanic phytoplankton. The present day sink for atmospheric CO_2 created by the growth of land plants has attracted much attention. What about oceanic phytoplankton? The amount of carbon dioxide fixed annually by photosynthesis in the sea is about the same as on land, but no forests are created since the typical cells are astonishingly small. Moreover forests on land experience a stimulus to growth from the increasing levels of atmospheric CO_2, and from deposition of fixed nitrogen from industrial activity. In the ocean dissolved CO_2 is everywhere in very large quantities, and can not be limiting to plant growth. Yet growth does appear to be limited in some way, for satellite observations of ocean color show that vast areas of blue water occur where we know that large quantities of nitrate and phosphate are present in the sunlit zone. Why is this so?

The iron hypothesis. It fell to the genius of John Martin to ask and answer this question. The traditional view had been the equivalent of the land observation that grazing by sheep can keep the grass short ñ the chlorophyll levels in these waters were very low supposedly due to the rapid grazing of microscopic marine animals. Martin suggested, based upon demanding laboratory measurements, that truly trace quantities (10^{-9}—10^{-12}M) of iron were lacking. He predicted that addition of trace iron levels to high nutrient-low chlorophyll ocean surface waters would stimulate a phytoplankton bloom, and thus photosynthetically fix carbon, lowering ocean surface CO_2 levels, and drawing in atmospheric CO_2 by gas exchange in large quantities. The idea met resistance, but was tested (22) in a superb field experiment in 1993 at a location 500 km south of the Galapagos Islands. Tragically John Martin died before seeing the success of his experiment.

The results of the experiment were clear. A 64 km^2 region of the open ocean was induced to yield a doubling of plant biomass, a threefold increase in chlorophyll, and a fourfold increase in plant production, all by the simple and elegant addition of a dilute tracer cloud of iron. The authors of this paper were however obliged to state that "Such experiments are not intended as preliminary steps to climate manipulation." This statement arose from contentious debate well before the experiment was ever executed.

In the struggle to gain recognition for his published ideas Martin had appeared on national television and uttered the phrase "Give me a tanker of iron and I'll give you an ice age," drawing upon his belief of the role of iron limitation in CO_2 changes of climates past. This radical idea naturally drew fire, and serious questions were raised. The debate focused on the possibility of making use of the vast area, and quantities of unutilized nutrients, found in the Antarctic circumpolar region. Earlier papers had pointed to changes in ocean chemistry here as being possibly linked to changing atmospheric CO_2 levels associated with the ice ages.

The criticisms of this ingenious idea (23, 24) focused on moving beyond the role of biology to formally incorporating ocean dynamics in box model simulations calibrated by tracer data. It is necessary not just to fertilize a patch of ocean, but to remove the fixed carbon from atmospheric return by ocean mixing, and to bring new nutrient rich water back to the surface and repeat the cycle. Calculations showed that even if the proposed iron fertilization of the entire Southern Ocean (16% of the world ocean surface) was highly successful in removing all nutrients and their corresponding fixed carbon then after 100 years of constant fertilization the atmospheric CO_2 levels would be about 90-107 p.p.m.v. less than the "Business as Usual" scenario. Still, carbon removal on a scale of Gt/year might be possible by such a massive effort.

The success of the first oceanic iron enrichment experiment lead to a larger and more elegant equatorial Pacific follow-on study in 1995 (25). Here a massive phytoplankton bloom was created in an 8 km x 8km

patch through a more careful series of trace iron additions, and a much larger draw down of about 90 p.p.m.v. in ocean surface CO_2 levels (Figure 6) was created (26). The "iron hypothesis" now moved to the status of the "iron theory" and the authors (25) now argued that fluctuations in atmospheric iron deposition on the ocean surface could indeed have created changing atmospheric CO_2 levels during glacial periods. The implications for the widely discussed climate controls were thus obvious.
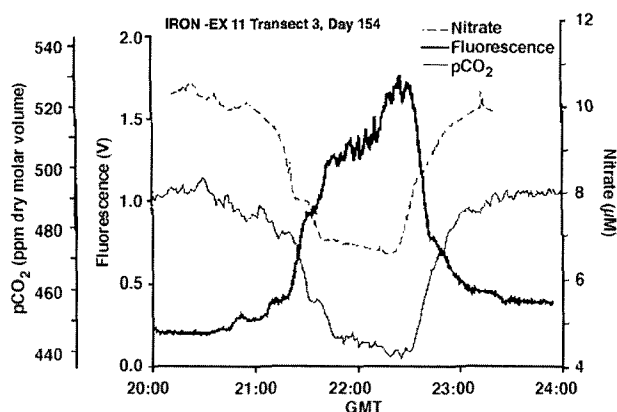

Figure 6. The values of pCO_2, NO_3, and the fluorescence of chlorophyll across the patch of water fertilized by the trace addition of iron during the IRONEX II study (25). Note the strong removal of nutrients and the draw-down of CO_2 caused by the strong growth of phytoplankton. From Millero (27).

If atmospheric CO_2 levels are to be manipulated in this way then the vast areas of the southern ocean must be called into play. The enhanced vertical mixing there, the violent storms, and the lack of winter light are all negatives for sustaining stable plant growth. Nonetheless a successful short-term iron fertilization experiment in these waters has recently been reported.

Assessment. The situation here is now changing rapidly, and is being aggressively pursued by entrepreneurs. A patent on iron fertilization of the ocean on a massive scale as a "Method of Improving the Production of Seafood" has been awarded, but this also makes reference to the removal of CO_2 from the atmosphere. There are a great many reasons to be cautious here.

The nature of oceanic carbon cycling is that the vastly greater amount of carbon and nutrients fixed at the surface is returned as CO_2 by grazing of microscopic animals within very short time and length scales. Thus a build up of CO_2, and a deficit of oxygen, occurs within the shallow ocean waters. The iron however is not soluble and is readily adsorbed onto the surfaces of sinking particles and transported to depth. We thus have a Faustian bargain, where the iron must be added again within a short time, and then for year after year to maintain the gradient. And if we ever stop then atmospheric CO_2 levels will in short time rise back and undo much of our work. The cost and the energy penalty of CO_2 removal by this strategy may be superficially less than direct injection, but the carbon credits are fleeting. The projected interference with ecosystems is massive, and it would occur over vast areas of the earth's surface.

The insights gained by these studies into the controls on ocean biogeochemistry are compelling, and further beautiful perturbation experiments will surely follow. But the industrial use of this strategy on any scale comparable to the carbon requirements for atmospheric stabilization is open to very serious challenge.

Summary

The scientific process of measure, model, and warn is of course essential. How else are we to perceive danger, or tell if any mitigation strategy is working? But the need to face up to sequestration as one option may come quite soon. The UNFCCC Kyoto Protocol is a work in progress, and we make expect significant modifications. But the idea of a binding numerical target for emissions is likely to endure. The initial reporting period was set for 2008–2012, those dates are fast approaching, and the U.S. is not now on track for meeting these goals.

The solution of purchasing carbon credits from other nations is expensive (28) and will only make sense if it leads to real geophysical change. These are billion dollar issues, the problem of monitoring for national emissions, and for carbon credits for land-use change, is daunting, and may not even be possible with systems in place today.

Yet if an effective sequestration technology can be devised then our ability to continue use of the fossil fuels that supply abundant energy for our economy will be preserved. In a sense this may be the price we pay for living in a technologically advanced society. We have long enjoyed the public health benefits from taking care of sanitary waste, and the disposal of municipal waste now ranks high as a societal benefit. We will likely have to take more complex measures to dispose of our energy wastes in the coming century. Domestic technologies such as these could be developed to help meet numerical emissions targets in place of purchase of carbon credits abroad.

The ocean science behind the two options described here is quite different, one involving new discoveries of the biogeochemical cycles of the sunlit surface ocean over enormous areas, and one involving the novel and strange physical chemistry of fluids and carbonate sediments at specific locations at great depths. Both are intimately linked to advances in ocean physics on all scales, and to careful environmental scrutiny. These processes are not mutually exclusive, and each can be explored simultaneously as we seek the soundest science and the most effective path. These are of course not the only ocean options, for example the use of carbonate mineral dissolution at the power plant by the effluent gas, followed by ocean disposal of the bicarbonate waste stream, has also been considered (29).

These ideas and innovative tests can only have arisen from the wise investment in ocean science made over the last few decades. The superb advances in trace metal chemistry, and ocean modeling, in the new blend of "biogeochemical," in ocean physics and the carbon cycle, the science of tracers, and in deep-sea vehicle technology have all been critical. Perhaps foremost has been the ethic of testing new ideas in the real world of science at sea, and of letting nature tell us the truth. I think Roger would have liked that.

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REFERENCES

(1) Callendar, G.S., 1938. *Q. J. R. Meteorol. Soc.*, 64, 223-240.

(2) Munk, W.H., 1997. *Proc. Natl. Acad. Sci.*, 94, 8275-8279.

(3) Revelle, R. and H.E. Suess, 1957. Tellus IX, 18-27.

(4) IPCC Working Group 1,1996: *Climate Change 1995: The Science of Climate Change.* Cambridge Univ. Press, 572 pp.

(5) Mann, M.I., R.S. Bradley and M.K. Hughes, 1999. *Geophys. Res. Lett.*, 26, 759-762.

(6) Wigley, T.M.L., R. Richels and J.A. Edmonds, 1996. *Nature*, 379, 240-243.

(7) U.S. Department of Energy, 1999: *Working Paper on Carbon Sequestration Science and Technology.*

(8) Panel on Policy Implications of Greenhouse Warming, 1992: *Policy Implications of Greenhouse Warming: Mitigation, Adaptation, and the Science Base.*

National Academy Press, 918 pp.

(9) Fan, S., M. Gloor, J. Mahlman, S. Pacala, J. Sarmiento, T. Takashi, and P. Tans, 1998. *Science*, 282, 442-446.

(10) Holland, E.A. and S. Brown, 1999. *Science*, 283, 1815.

(11) Potter, C.S. and S. Klooster, 1999. *Science*, 283, 1815.

(12) Marchetti, C., 1977. *Climate Change*, 1, 59-68.

(13) Handa, N. and T. Ohsumi, 1995: *Direct Ocean Disposal of Carbon Dioxide.* Terra Scientific Publishing, Tokyo, 274 pp.

(14) Brewer, P.G., 1997. *Geophys. Res. Lett.*, 24, 1367-1369.

(15) Stuiver, M., P.D. Quay, and H.G. Ostlund, 1983. *Science*, 219, 849-851.

(16) Brewer, P.G., G. Friederich, E.T. Peltzer and F.M. Orr Jr., 1999. *Science*, 284, 943-945.

(17) Hanisch, C., 1998. *Environ. Sci. Tech.*, 32, 20A-24A.

(18) Brewer, P.G., F.M. Orr Jr., G. Friederich, K.A. Kvenvolden and D.L. Orange, 1998. *Energy & Fuels*, 12, 183-188.

(19) Robbins, P.E. and W.J. Jenkins, 1998. *J. Mar. Res.*, 56, 1125-1161.

(20) Haugan, P.M. and H. Drange, 1992. *Nature*, 357, 318-320.

(21) Archer, D., H. Kheshgi and E. Maier-Reimer, 1998. *Global Biogeochem.* Cycles 12, 259-276.

(22) Martin, J.H. et al., 1994. *Nature*, 371, 123-129.

(23) Peng, T.-H. and W.S. Broecker, 1991. *Nature*, 349, 227-229.

(24) Joos, F., J.L. Sarmiento and U. Siegenthaler, 1991. *Nature*, 349, 772-775.

(25) Coale, K.H. et al., 1996. *Nature*, 383, 495-501.

(26) Cooper, D.J., A.J. Watson and P.D. Nightingale, 1996. *Nature*, 383, 511-513.

(27) Millero, F.J., 1996. *Chemical Oceanography.* CRC Press, 469 pp.

(28) Cooper, R.N., 1998. *Foreign Affairs*, March/April, 66-79.

(29) Rau, G.H. and K. Caldeira, 1999. *Energy Convers. Mgmt.*, 40, 1803-1813.