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Beyond Climate: The Emerging Science of a Low pH-High CO_2 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 places 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 CO_2 levels have received great attention, the direct effects of the enormous CO_2 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 CO_2 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 CO_2 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 CO_2 status of the worlds oceans began.

The scientific attacks described above basically treated the CO_2 transient as a "tracer" problem. That is the chemical complexity of CO_2 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 CO_2 signal was then inferred from these proxy measurements.

The ocean absorption of fossil fuel CO_2 is a function of sea water alkalinity. In the very simplest terms carbonic acid, formed by dissolution of CO_2 in water, reacts with calcium carbonate dissolved in a slightly alkaline ocean to form bicarbonate. The result is an elevation of ocean CO_2 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*CO2 and *f*CO2, 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:

$$\Delta TCO_2 = 0.8297\Delta O_2 + 0.5\Delta TA$$

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

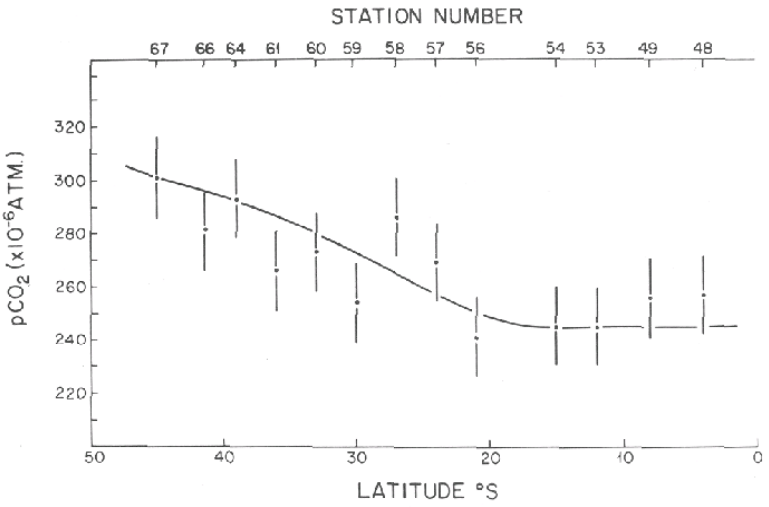

Fig. 2. The calculated initial pCO_2 of samples taken at the core of the salinity minimum of the Antarctic Intermediate Water in 1972.

Figure 1. A copy of Fig. 2 from Brewer (1978) showing the first attempt to recover the oceanic fossil fuel CO2 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 CO_2 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 CO_2 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 CO_2 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 JGOS/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 CO_2 signal accumulated from 1800 to 1994 is 118 ± 19 petagrams of carbon; this is 433 billion metric tons of CO_2, 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 CO_2 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 CO_2 across the ocean surface is estimated as ~2 petagrams C/year (IPCC, 1995) or ~7 billion tons CO_2 per year. Thus in the decade since 1994 we have added an additional ~ 70 billion tons CO_2, and the accumulated ocean burden must therefore be about 500 billion tons at the time of giving this lecture. Since the atmospheric CO_2 level has risen in the last ten years, the oceanic invasion rate has risen also, and thus the oceanic invasion rate of fossil fuel CO_2 must now be close to 1 million tons CO_2 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 CO_2 levels within the next few decades (Hoffert et al., 2002).

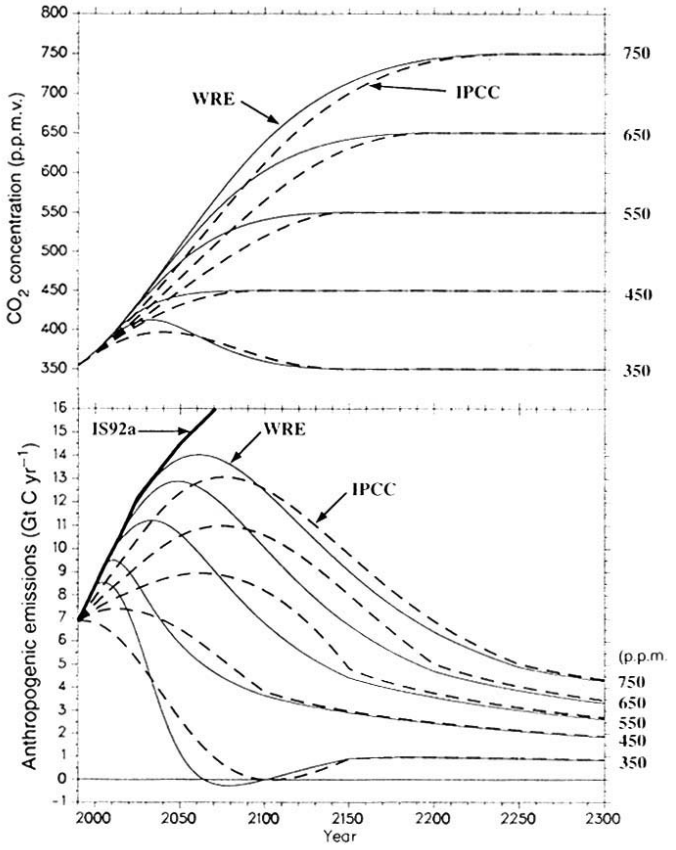

Fig. 2. A version of the IPCC IS92a emissions scenario (bold line, lower panel), together with pathways for atmospheric CO_2 stabilization as modeled by IPCC and by Wigley et al. (WRE). From Wigley et al. (1996). The difference between the IS92a scenario and the stabilization curves indicates the magnitude of the changes required to stabilize CO_2 levels.

A very large fraction of the available fossil fuels will be burned, and the CO_2 transferred to the ocean. The principal uncertainty is in the time scale, and the usually unspoken assumption behind plans for slowing fossil fuel CO_2 emissions to moderate climate change is to give more time for the ocean to absorb the excess CO_2. In short, all nations whether maritime or landlocked, count on ocean surface CO_2 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 CO_2 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 CO_2 chemistry predicted are shown in the table below.

It is clear that by mid-century or shortly thereafter we could approach atmospheric CO_2 levels of ~600 ppm, and thus surface ocean chemistry changes of $\Delta pH \cong 0.3$. By the end of this century far larger changes are possible. Of critical concern is the change in carbonate ion [$CO_3^{=}$] 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"

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

Fig. 3. From Brewer, 1997. The table shows the calculated changes in ocean CO_2 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 $CO_3^{=}$ 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 CO_2 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 CO_2 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 CO_2, 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 CO_2 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 CO_2 in the Ocean

Once CO_2 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 CO_2 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 CO_2 are disposed of in the ocean anyway this may be seen as simply accelerating a "natural" process in which mankind first disposes of CO_2 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 CO_2 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 CO_2 and CH_4 will form a solid hydrate ($Gas.6H_2O$) 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 CO_2 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 CO_2 hydrates (Brewer et al., 1998). We now know both from empirical reasoning, and from experiment (Rehder et al., 2004) that CO_2 hydrate will dissolve quite rapidly in sea water since the aqueous phase is enormously under saturated with dissolved CO_2.

Modeling of the fate of CO_2 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 CO_2 enriched water in the Antarctic upwelling region after some centuries of isolation from the atmosphere will result in some return of CO_2 from ocean to atmosphere, followed by re-absorption by the ocean. The expected result is "peak shaving" of the anticipated atmospheric CO_2 signal.

Carrying out ocean CO_2 experiments

The physical behavior of CO_2 in sea water is complex, and experimental advances were thus dependent on advances in technique. The first controlled CO_2 injection experiment (Brewer et al., 1998) relied upon helium pressure to expel liquid CO_2. This was not ideal due to the finite solubility of He in CO_2, and purely mechanical accumulator containment and delivery systems were soon developed (Brewer et al., 1999). CO_2 exists in the liquid state below depths of ~400m for typical oceanic conditions. It is a highly compressible fluid, and thus it's 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 HCO_3^- and $CO_3^=$ that characterize the dissolved ocean CO_2 system and indicate its pH.

Models show that the time of ocean retention of injected CO

Conclusions

I have attempted to present, in somewhat narrative form, an account of the progress in ocean CO_2 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 CO_2 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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References

Barry, J.P., K.R. Buck, C.F. Lovera, L. Kuhnz, P.J. Whaling, E.T. Peltzer, P. Walz, P.G. Brewer, 2004. Effects of direct ocean CO_2 injection on deep-sea meiofauna. Journal of Oceanography, 60, 759-766.

Brewer, P.G., 1978. Direct observation of the oceanic CO_2 increase. Geophysical Research Letters 5, 997-1000.

Brewer, P.G., 1997. Ocean chemistry of the fossil fuel CO_2 signal: The haline signature of "Business as Usual". Geophysical Research Letters 24, 1367-1369.

Brewer, P.G., Orr, F.M. Jr., Friederich, G., Kvenvolden, K.A., and Orange, D.L., 1998 Gas hydrate formation in the deep sea: *In situ* experiments with controlled release of methane, natural gas and carbon dioxide. Energy and Fuels, 12, 183-188.

Brewer, P.G., Friederich, G., Peltzer, E.T., and Orr, F.M. Jr., 1999. Direct Experiments on the Ocean Disposal of Fossil Fuel CO_2. Science, 284, 943-945.

Brewer, P.G., 2000. Contemplating action: Storing carbon dioxide in the ocean. Oceanography, 13, 84-92.

Callendar, G.S., 1938. The artificial production of carbon dioxide and its influence on temperature. Quarterly Journal of the Royal Meteorological Society 64, 223-240.

Chen, C.-T. and Millero, F., 1979. Gradual increase of oceanic CO_2. Nature 277, 205-206.

Cicerone, R., Orr, J., Brewer, P.G., Haugan, P., Merlivat, L., Ohsumi, T., Pantoja, S., and Portner, H.O., 2004. The ocean in a high CO_2 world. Eos, 85, 351-353.
DeLucia, E. H., J.G. Hamilton, S.L. Naidu, R.B. Thomas, J.A. Andrews, A. Finzi, M. Lavine, R. Matalama, J.E. Mohan, G.R. Hendrey, and W.H. Schlesinger, 1999. Net primary production of a forest ecosystem with experimental CO_2 enrichment. *Science*, 284, 1177- 1179.

Field, C.B. and Raupach, M. 2004. The Global carbon Cycle. Island Press, 526pp.

Forch, C., Knudsen, M. and Sorensen, S.P.L., 1902. Berichte uber die Konstantenbestimmungen zur Aufstellung der hydrographischen Tabellen. Kgl. Danske Videnskab. Selskabs Skrifter, 7 Rackke, Naturvidensk. Og Mathem. Afd. 12, 1-151.

Gale, J. and Kaya, Y., Eds., 2003. Greenhouse gas control technologies. Pergamon Press, 2 volumes, 1879 pp.

Gruber, N.L., Sarmiento, J.L., and Stocker, T.F., 1996. An improved method for detecting anthropogenic CO_2 in the oceans. Global Biogeochemical Cycles 10, 809-837.
Knudsen, M., 1901. Hydrographische Tabellen. G. E. C. Gad, Copenhagen, 63p.

Haugan, P. and Drange, H., 1996. Effects of CO_2 on the ocean environment. Energy Conversion Management 37, 1019-1022.

Haugan, P., 2003. On the production and use of scientific knowledge about ocean sequestration. In: Greenhouse Gas Control Technologies. J. Gale and Y. Kaya, Eds., Pergamon Press, 719-724.

Hoffert, M. and 17 others, 2002. Advanced technology paths to global climate stability: Energy for a greenhouse planet. Science 298, 981-987.

Houghton, J.T., Filho, L.G.M., Bruce, J., Lee, H., Callander, B.A., Haites, E., Harris, N., amd Maskell, K., eds. 1995. Climate change 1994: Radiative forcing of climate change and an evaluation of the IPCC IS92 emissions scenarios. Cambridge University Press.

Johnson, K.S., 1982. Carbon dioxide hydration and dehydration kinetics in sea water. Limnology and Oceanography, 27, 849-855.

Kleypas, J.A., Buddemeier, R.W., Archer, D., Gattuso, J.P., Langdon, C., and Opdyke, B.N., 1999. Geochemical consequences of increased atmospheric carbon dioxide on coral reefs. Science, 284, 118-120.

Kurihara, H., Shimode, S., and Shirayama, Y., 2004. Sub-lethal effects of elevated concentrations of CO_2 on planktonic copepods and sea urchins. Journal of Oceanography, 60, 743-750.

Langdon, C., T. Takahashi, C. Sweeney, D. Chipman, J. Goddard, F. Marubini, H. Aceves, H. Barnett, and M.J. Atkinson (2000) Effect of calcium carbonate saturation state on the calcification rate of an experimental coral reef. *Global Biogeochem. Cycles* **14** 639-654.

Marchetti, C., 1977. On geoengineering and the CO_2 problem. Climatic Change, 1, 59-68.

Nakayama, N., E.T. Peltzer, P. Walz, and P.G. Brewer, 2004. First results from a controlled deep-sea CO_2 perturbation experiment: evidence for rapid equilibration of the oceanic CO_2 system at depth. Journal of Geophysical Research, Submitted.

Oeschger, H., Siegenthaler, U., Schattere, U., and Gugelman, A., 1975. A box diffusion model to study the carbon dioxide exchange in nature. Tellus 27, 168-191.

Orr, J.C. and 13 others, 2003. The GOSAC project to predict the efficiency of ocean CO2 sequestration using 3-D ocean models. In: "Greenhouse Gas Control Technologies. J. Gale and Y. Kaya, Eds., Pergamon Press, 1691-1694.

PCAST (President's Council of Advisors on Science and Technology), 1997. Federal Energy Research and Development Agenda for the Challenges of the Twenty-First Century. U.S. Dept. of Energy, Washington, D.C., November.

Portner, H.O., Langenbruch, M., and Reipschlager, A., 2004. Biological impact of elevated ocean CO_2 concentrations: Lessons from animal physiology and earth history. Journal of Oceanography, 60, 705-718.

Rehder, G., Kirby, S.H., Durham, W.B., Stern, L.A., Peltzer, E.T., Pinkston, J. and Brewer, P.G., 2004. Dissolution rates of pure methane hydrate and carbon dioxide hydrate in under-saturated seawater at 1000m depth. Geochimica et Cosmochimica Acta., 68 (2), 285-292.

Revelle, R. and Suess, H.E., 1957. Carbon dioxide exchange between atmosphere and ocean and the question of an increase of atmospheric CO_2 during past decades. Tellus 9, 18-27.

Riebesell, U., Zondervan, I., Rost, B., Tortell, P.D., Zeebe, R., and Morel, F., 2000. Reduced calcification of marine plankton in response to increased atmospheric CO_2. Nature, 407, 364-367.

Sabine, C.L. and 14 others, 2004. The oceanic sink for anthropogenic CO_2. Science 305, 367-371.

Seibel, B. and Walsh, P.J., 2001. Potential impacts of CO_2 injection on deep-sea biota. Science, 294, 319-320.

Seibel, B. and Walsh, P.J., 2003. Biological impacts of deep-sea carbon dioxide injection inferred from indices of physiological performance. The Journal of Experimental Biology, 206, 641-650.

Shaw, H. R., E.S. Zavaleta, N.R. Chiariello, E. L. Cleland, H.A. Mooney, and C.B. Field, 2002. Grassland responses to global environmental changes suppressed by elevated CO_2. Science, 298, 1987-1990.

Tamburri, M., E.T. Peltzer, G. Friederich, I. Aya, K. Yamane, and P.G. Brewer, 2000. A field study of the effects of CO_2 disposal on mobile deep-sea animals. Marine Chemistry 72, 95-101.

Wallace, D. W. R., 2001. Storage and transport of excess CO_2 in the oceans: The JGOFS/WOCE global CO_2 survey. In "Ocean Circulation and Climate", Academic Press, 489-521.

Wickett, M.E., Caldeira, K., and Duffy, P.B., 2004. High-resolution simulations of oceanic direct injection of anthropogenic CO_2 and CFC uptake. Journal of Geophysical Research, In Press.

Wigley, T.M.L., Richels, R. and Edmonds, J.A., 1996. Economic and environmental choices in the stabilization of atmospheric CO_2 concentrations. Nature 379, 240-243.