**Climate Change and Biodiversity in Melanesia**

**Biophysical Science - Ocean Acidification**

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**Synopsis**

The lowering of upper ocean pH from the now massive invasion of atmospheric fossil fuel $CO_2$ is an uncontested reality. We have already disposed of some 530 billion tons of fossil fuel $CO_2$ by gas exchange with the atmosphere, and the invasion rate today is some 24 million tons per day. This massive removal of $CO_2$ from the atmosphere is essential for our fossil fuel economy, for without ocean $CO_2$ uptake we would already have large-scale climate change today. The mean ventilation age of the deep waters of the world ocean (the mean time for re-exposure to the atmosphere) is about 575 years and thus we can count on ocean uptake of $CO_2$ for some centuries to come. Eventually some 85% of all atmospheric $CO_2$ emissions will reside in the ocean as air and sea reach equilibrium. This sets limits on allowable accumulated $CO_2$ emissions if a goal of stabilizing $CO_2$ levels is set. For example if the atmosphere is held stable at 550 ppmv $CO_2$ for several centuries we will transfer 6.2 trillion tons of $CO_2$ to the ocean at which time equilibrium between air and sea will be achieved, and zero fossil fuel $CO_2$ emissions to the atmosphere would be allowed. The political acceptability of this is unknown.

But the transfer of such extraordinary quantities of $CO_2$ comes at an ecological price, and that price is only now becoming examined and has yet to be fully established. In pre-industrial times the pH of the surface ocean varied about 8.2; today the mean value is about 8.1, and if reasonable predictions $CO_2$ emissions are followed then by the end of this century we will have lowered pH by about 0.4 units. This will result in the loss of about 55-60% of the dissolved carbonate ion that calcifying organisms (corals, sea urchins, calcareous phytoplankton etc) use to build their shells. But while the first-order chemical changes are known and directly predictable, the impact on marine organisms is far less certain, and the ability of animals to adapt to and cope with the stress imposed by higher $CO_2$ levels is to a significant degree unknown. For example while the annual growth rings of corals record with great fidelity the carbon isotope shifts of the 20$^{th}$ century, no record of thinning of these rings from the pH/carbonate ion reduction experienced so far has yet been reported.

While the immediate focus on lowered ocean pH and reduced carbonate ion concentration is understandable, far more complex and widespread issues are quickly emerging. The dissolved $CO_2$ content will probably rise by about 12%, with increasing stress on the respiration and reproduction of deep-sea animals. Added to the purely inorganic addition of $CO_2$ from fossil fuels will be the stress of lowered oxygen and higher respiratory $CO_2$ in the deep-sea from higher temperatures and lowered atmospheric ventilation. The result will be greatly expanded ocean sub-oxic regions.

The rapidly emerging set of papers and reports on ocean impacts that are now appearing needs care in interpretation since standard protocols are not yet in place, and there are gaps in many model assumptions. For example the common use of acid addition to achieve lowered sea water pH for experiments, rather than the more complex addition of $CO_2$ itself, can easily create artifacts. We know far too little about the response of modern marine animals to the epochal-scale changes in the ocean that are occurring and their ability to cope with the combined physiological stresses of temperature, $CO_2$, and lowered oxygen levels now being imposed. Experimental protocols for true field $CO_2$ enrichment techniques are only now being developed, and the genetic resources possessed by marine animals to cope with such changes are still unknown.

## Introduction

Awareness of ocean acidification, the lowering of the pH of sea water from the steadily increasing invasion of atmospheric fossil fuel $CO_2$ by gas exchange across the air-sea boundary, has now risen in both the public mind and the science community as an apparently new phenomenon of concern, with likely negative impacts on coralline systems such as those throughout Melanesia being widely debated. What is the background to this, how solid are the observations and projections, and are the possible impacts in all their complexity foreseeable? And are there ways out of this bind, modes of adaptation, and possible ameliorating strategies?

### A Brief History

The current and impressive stream of reports (Cicerone et al., 2004; Royal Society, 2005; Kleypas et al., 2006; WBGU, 2006) workshops and extensively multi-authored papers (e.g. Orr et al., 2005) on ocean acidification can be traced to the seminal meeting held in Paris in May 2004 under the auspices of the Intergovernmental Oceanographic Commission (IOC) and the Scientific Committee for Ocean Research (SCOR). Originally planned as a forum to debate direct ocean $CO_2$ sequestration, the focus of the meeting was changed at a planning session held at the NAS Beckman Center in February, 2003 to reflect very real concern over the massive ocean invasion signal.

In fact geochemical knowledge of oceanic uptake of fossil fuel $CO_2$ by alkaline sea water has a far longer and impeccable history; it is odd that that the biological impacts have been so slow in recognition. Callendar (1938) recognized that "the rate at which sea water could correct an excess of atmospheric carbon dioxide depends mainly upon the fresh volume of water exposed to the air each year", but with the knowledge of ocean mixing rates available at that time assumed a rather rapid ocean uptake – and slower accumulation in the atmosphere than we have today. In the post World War II renaissance of geophysical science Revelle and Suess (1957) revived this theme, and by using the power of the newly available $^{14}C$ data they estimated that the ocean would take up annually some 40% of the $CO_2$ emissions. Dubbed as a "natural" process, the oceanic sink was regarded by many as the savior from the atmospheric $CO_2$/global warming problem, and that indeed is its critical role. But the oceanic uptake blessing comes at a price, and that price is now being uncovered.

In the long run the ocean will take up some 85% of all mankind's fossil fuel $CO_2$ emissions. The basic rules for this were elegantly established by Sillen (1961), in which the chemistry of the ocean was seen as "the result of a gigantic acid-base titration: acids that have leaked out from the interior of the Earth, HCl, $H_2SO_4$, $CO_2$, are titrated with bases that have been set free by the weathering of primary rock. In this acid-base titration, volcanoes against weathering, it would seem that we are about 0.5% from the equivalence point." In the short term (days to centuries) ocean uptake is governed by the reaction of $CO_2$ with the already dissolved calcium carbonate in sea water to form bicarbonate. We are now using up that store of dissolved carbonate ion. In the long run, hundreds of thousands of years, that will be replenished by rain water falling on e.g. the granites of Yosemite which contain oxides of sodium, potassium etc., and creating the alkalis which will slowly restore ocean geochemistry.

Thus when curbs on atmospheric emissions today are urged, the rationale is often given that this will allow time for "natural processes to catch up"; that process is dominantly ocean uptake by gas exchange. Rates of ocean uptake are therefore of key importance, and these are now well known. The modest computational facilities available to Callendar, and to Revelle and Suess, led them to consider the ocean essentially as a giant well-mixed geochemical box, and rates were unreasonably fast. Oeschger et al. (1975) initiated the modern resolution of this problem by developing a multi-layered box-diffusion model, tuned by the observed $^{14}C$ signal. This led to more reasonable uptake rates, around 36% of atmospheric input annually. Today we live in an age of huge and sophisticated global computer models of ocean physical mixing reduced to finer scales, and ocean uptake rates are estimated as about 30-33% of emissions annually (IPCC, 2007).

But the underlying insights into geochemistry have remained firm for half a century and are unchallenged.

## The signal today

What then is the situation today? The large and variable natural background of dissolved $CO_2$ in the ocean is steadily being overwritten by the fossil fuel $CO_2$ invasion from above. Brewer (1978) first devised a protocol for recovering the fossil fuel $CO_2$ signal from the oceanic background, but imperfections in the data and analytical procedures caused concern over the validity of the signal. These issues were resolved (Bradshaw et al., 1981), far better data sets resulted, and modifications in extracting the signature of the fossil fuel invasion over the last 30 years, primarily to account for small surface water disequilibria (Gruber et al., 1996), now show directly from analysis of global survey data the massive fossil fuel $CO_2$ invasion in great detail (Sabine et al, 2004).

The result is that an accumulation of some 530 billion tons of fossil fuel $CO_2$ has been transferred to the upper ocean, and that this signal can be traced down to more than 1km depth over the entire world ocean (Sabine et al., 2004). Figure 1 shows the accumulation recorded from expeditions in the late 1980s to early 1990s.

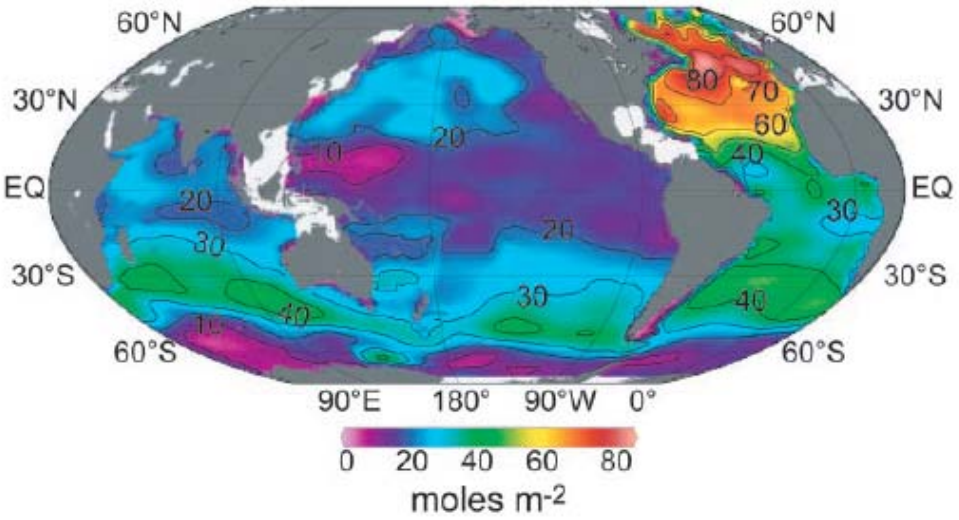


**Fig. 1.** Column inventory of anthropogenic $CO_2$ in the ocean (mol $m^{-2}$). High inventories are associated with deep water formation in the North Atlantic and intermediate and mode water formation between 30° and 50°S. Total inventory of shaded regions is 106 ± 17 Pg C.

From Sabine et al., 2004.

**Overview of the science**

The biological effects of this extraordinary change in the chemistry of sea water are now being widely investigated. The changes are of geologic scale, and are happening with a rapidity unseen on Earth for many millions of years (perhaps never).

Ocean chemists measure the sea water mass properties of total $CO_2$ and alkalinity for fundamental reasons, but it is the translation to the computed property of pH that finally attracted the attention of marine physiologists. Simple calculations show (e.g. Brewer, 1997) that present day surface ocean water is reduced in pH by about 0.1 units relative to pre-industrial values, and that projections for the future indicate changes of 0.3 by mid-century, and by 0.4 by the year 2100. These are of a scale to cause concern for the basic functioning of many marine ecosystems.

One such projection is that of Orr et al. (2005) seen in Figure 2 below:

**Figure 2.** From Orr et al. (2005), showing increasing oceanic surface $CO_2$ and decreasing pH over the 21st century under two IPCC scenarios for fossil fuel $CO_2$ emissions. The resulting change in the saturation state of calcite and aragonite is also shown, indicating actual aragonite under-saturation in the southern ocean at the end of this century

The initial focus on the reduction in carbonate ion, and the decreasing saturation state of calcite and aragonite, is understandable since these are obvious concerns (Kleypas et al., 2006) and since coralline ecosystems are so widely known and treasured (Hoegh-Guldberg et al. 2007). The rate of change alone is astonishing.

**Table 1.** From Hoegh-Guldberg et al. (2007). The predicted rate of change of $CO_2$ and temperature under two IPCC emission scenarios compared to the ice core record of the last 420,000 years, and the observed record of the last 136 years.

Thus early experimental work focused on these systems (Langdon et al., 2004) with the result that a reduction in calcification rate in an experimental ecosystem of about 40% for a doubling of $CO_2$ was found. This change in pH, coupled with the climatic rise in temperature and associated coral bleaching, will likely pose great stress for coral reef systems in the next few decades.

This theme, of reduced carbonate ion and therefore stress on calcification, has now resulted in very large literature. Stress on calcifying phytoplankton from mesocosm experiments (Zondervan et al., 2001), on sea urchin development (Kurihama and Shirayama, 2004), and on many other marine organisms has been shown. For an extreme case Fine and Tchernov (2007) report the experimental complete denuding of a scleractinian coral by exposure to pH 7.3 to 7.6 sea water for a year, followed by re-growth of the calcified skeleton on re-exposure to normal sea water.

The issue of calcification is by no means the only concern. More generally almost all physiological processes for higher marine animals are negatively affected by higher $pCO_2$ levels; the question is to what degree, and on how effectively animals may be able to compensate. This topic was reviewed in the IPCC Special Report on Carbon Capture and Storage which considered direct deep ocean $CO_2$ injection as a possible sequestration option (IPCC, 2005). An excellent account is given in recent work by Portner et al. (2004) and Portner (2008).

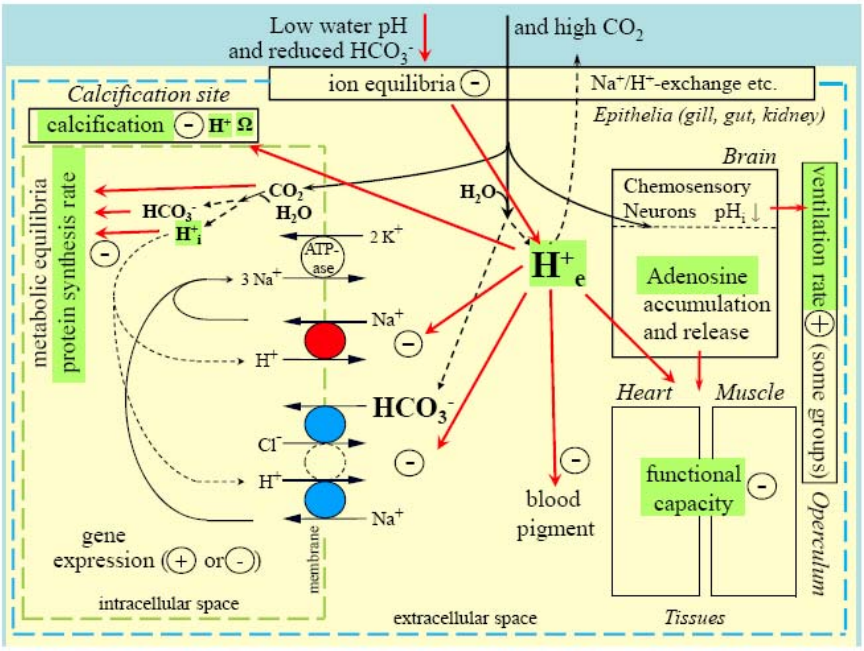


**Figure 3.** From Portner (2008). Generalized physiological diagram showing the complex of cellular processes involving $CO_2$ and acid-base functioning in a marine animal.

The complexity of the physiological diagram above requires interpretation. In the very simplest terms it is more difficult for an animal to respire at lower $O_2$ and higher $CO_2$ levels, thus imposing an energy burden, and reducing the resources available for essential functions such as locomotion and reproduction. With rising temperatures, and lower dissolved oxygen, these stresses could become acute particularly in the oxygen minimum zone a few hundred meters below the sea surface where conditions for the support of marine life are already marginal.

The essential interaction between marine geochemists and physiologists has been too slow in development and communication has been hampered. Basic issues such as use of

common units and lack of knowledge of essential literature remain. Most of the focus has been on changes in surface ocean chemistry; but changes in the deep water will be far more pronounced though slower in appearing. For example a change in atmospheric $pCO_2$ will produce an almost equivalent $pCO_2$ change in surface waters. But when the added mass of $CO_2$ is advected to depth and undergoes the biogenic removal of $O_2$ and addition of respiratory $CO_2$ the chemical change is considerably amplified. A change of +280 ppm $pCO_2$ (doubling the pre-industrial value) to surface waters can produce a change of +2,500 ppm $pCO_2$ at a few hundred meters depth in sub-oxic waters due the changes in buffer capacity of the fluid. The complex interaction of temperature, lowered $O_2$ and higher $pCO_2$ will be hard to define, but basically it will impose a fundamental energy constraint on marine animals that will greatly expand the regions of the world ocean that can thermodynamically be shown to not support marine life.

The ability of marine animals to cope with thermal stress is reduced under higher dissolved $CO_2$ levels, and so we may expect the thermal window within which an animal has adapted and can thrive will narrow. Climate change will force migration of species to higher latitudes to maintain their thermal optimum, and higher $CO_2$ levels will reduce the zones available (Portner and Knust, 2007).

There is increasing evidence that deep-sea species, adapted to a highly stable environment with very small changes in T and pH experienced for millennia are particularly sensitive to change (Pane and Barry, 2007) and are far more sensitive to changing $CO_2$ levels than are their shallower living counterparts. And for many species the impact of higher $CO_2$ levels on egg development and larval survival appears to be acute.

**Assessment of relative levels of certainty for various projections**

The assignment of uncertainty to these projections is often difficult, but more so for the ecological outcome than for the climate and $CO_2$ level projections.

The uncertainty over changes in physical climate has been extensively reviewed in the IPCC series of reports and need not be repeated here. For future $CO_2$ levels there are now many scenarios with an enormous range of projections (IPCC, 2000), but for convenience the so-called "Business as Usual" or IS92a scenario is most commonly used. That scenario predicts the lowering of ocean pH by 0.4 units by century end, and an atmospheric $CO_2$ doubling by mid-century, and as such it widely criticized as pathway to a climate crisis. In fact this projection is that of a technologically advanced and climate conscious society; it assumes for example that:

- In 100 years renewable and nuclear technologies will provide more than 75% of all electric power, compared to 24% in 1990
- Non-carbon technologies (including solar and wind) are assumed to grow to about twice the size of the entire global energy system in 1990
- Energy consumed per unit of economic activity will decline to 1/3 of 1990 levels.

These assumptions pose enormous technical and societal challenges, and we are proceeding far above that path today. Thus in spite of strong public awareness the projected $CO_2$ levels appear to be on the low side based upon outcomes of the 1990 to 2008 period.

The actual pH and $CO_2$ system changes that will be experienced in the sub-surface ocean appear to be significantly greater than those estimated above. Projections such as those of Caldeira and Wickett (2003) relying on the IS92a scenario are designed to show the impact of the fossil fuel $CO_2$ component alone. While that will be true for the surface ocean, the deeper waters will experience an additional strong perturbation from changes in physical circulation (reduced ventilation with the atmosphere), higher temperatures thus reducing $O_2$ solubility and increasing respiration rates. These effects will be large; there is an already observable trend towards decreasing $O_2$/higher $CO_2$ levels from these climate/ventilation/respiration changes, most easily observable in semi-isolated basins (Chen et al., 1999; Jenkins, 2008), but very likely proceeding world wide. I note that many marine animals make the daily vertical migration from day-time refuge to escape predation in such sub-oxic/high $CO_2$ waters to night-time surface

layers. Thus these large changes in the deeper $O_2/CO_2$ system are immediately relevant to ocean surface ecosystems.

Another layer of uncertainty comes from the inadequacy of much current experimental technique. Basically almost all experiments carried out today use of necessity short-term acute exposures to reveal effects. Scientists are well aware of the deficiencies here, but have as yet little choice. The more careful, longer term, slowly changing $CO_2$ level studies have yet to be done. More subtle but important is the widespread use of simple acid addition rather than $CO_2$ itself to control pH in experimental systems; this is not a true simulation and can cause errors. Some work on experimental mesocosms makes elegant use of direct $CO_2$ addition (e.g the series of papers by Riebesell and colleagues (Delille et al., 2005); others (Kuffner et al., 2007) use acid addition likely leading to some over-estimation of impacts.

A major source of uncertainty is the current need to carry out experiments in enclosed aquaria or mesocosms, where the natural system is not fully represented. The error introduced here is not known, but for $CO_2$ enrichment experiments on land the differences can be large. For example experiments on the supposed beneficial effects of higher atmospheric $CO_2$ levels on the growth of plants based upon greenhouse experiments which led to the unfortunate over-emphasis on forestation in the Kyoto protocol were undone by two decades of FACE (Free Atmosphere $CO_2$ Enrichment ) Experiments of many kinds (Long et al., 2006; Schimel, 2006). Equivalent in situ ocean $CO_2$ enrichment experiments are far more difficult but not impossible and active planning is now underway.

There are many examples of calcifying organisms surviving in lower pH environments, albeit with thinner shells and modified growth. Fresh/brackish water mussels and oysters offer one example. In the deeper ocean the cold water corals that thrive around the North Atlantic basin (Roberts et al., 2006) have been suggested as being greatly affected by ocean acidification. Yet in the Pacific their close cousins thrive atop sea mounts bathed in sea water well under-saturated with respect to aragonite; they appear to compensate well. One major difference is that in the Atlantic these systems often grow atop a bank of coralline debris; in the Pacific dead coralline material very rapidly dissolves.

One topic worthy of note is that although the annual growth rings of corals record with remarkable fidelity the carbon isotopic changes of the 20$^{th}$ century (bomb $^{14}C$, Suess effect) no thinning of annual growth rings from the pH changes experienced by the ocean so far have yet been reported.

Overall it appears that:

- The future changes in ocean $CO_2$ status may be underestimated given the present atmospheric trajectory, the rapidity of change, the economic challenge of changing this course, and the additional impacts of reduced ventilation and increased respiration.
- The combined effects of higher $CO_2$, higher temperature, and lower $O_2$ have not yet been adequately simulated in field experiments or models.
- Impacts on reproduction and embryonic and larval forms have not yet been fully investigated and there is evidence that these are the most sensitive life stages.
- But the ability of ecosystems to adapt to such changes, their resilience, or the co-opting of as yet unknown survival strategies is very much unexplored.
- Almost all work has been done at the organismal level – very little work on the genetic resources that may be available to marine populations has been carried out.

**Specific implications of ocean acidification for Melanesia**

It is difficult at this point to make any specific assessment for Melanesia, but the ability of the native coralline systems to adapt to such changes must be of primary concern. Ocean scientists do not have large and specific data bases for the region, and must rely on generalizations derived from broader scale surveys. This is unlikely to lead to major errors, but it

is a telling and disturbing gap that could be quickly filled in. Work now in the late planning stage for field $CO_2$-enrichment experiments could very well be considered for sites in Melanesia.

**Research needs**

Many of the recommendation for research have emerged from the discussion above:

- Longer term studies on full natural systems with true $CO_2$ enrichments for evaluating impacts
- Recognition of which species are the most likely to thrive, and predictions of change that allow intelligent and efficient monitoring for early detection
- Enhancement of any possible remediation strategies
- Economic and cultural adaptations to emerging changes

But basically the slowing of atmospheric $CO_2$ emissions is the only practical guard against change. Various proposals to increase ocean alkalinity or pH such a by passage of electric currents through a mesh over a coral reef, or by adding strong bases to the ocean, are fraught with truly major fundamental problems and would be of small scale.

In the matter of carrying out field experiments that could reliably predict the future of our high $CO_2$ ocean so that policy could be best informed of the impacts of our atmospheric $CO_2$ disposal habits it is important to look at the fundamental differences between land and ocean $CO_2$ enrichment techniques.

$CO_2$ enrichment experiments of very large scale to examine ecosystem responses have been carried out on land (Figure 4), but experiments of such scale are not possible in the ocean and very different constraints apply. These issues are now well understood and are further explored here.

**Figure 4.** A Free Air $CO_2$ Enrichment (FACE) experiment on forested land in Wisconsin.

$CO_2$ has no atmospheric chemistry so simple mixing of added $CO_2$ is all that is required for a land enrichment experiment. But $CO_2$ has a complex chemistry in sea water (Bradshaw et al., 1981; Millero, 2007) with multiple equilibria which are established at different rates; these rates are themselves a function of temperature and pH (Zeebe and Wolf-Gladrow, 2001). The solution of the kinetic equations is shown diagrammatically in Figure 5 with the e-folding time ( W) for the reaction on the y-axis. In practice this means:

i) That provision must be made for a significant lag time between the addition of $CO_2$ to sea water to allow the equilibrium signal to develop – a minimum of 2 W is desirable.

And

ii) That mixing with external sea water in the exposure chamber be minimized – the system should be bathed fully in the equilibrated $CO_2$ enriched fluid.

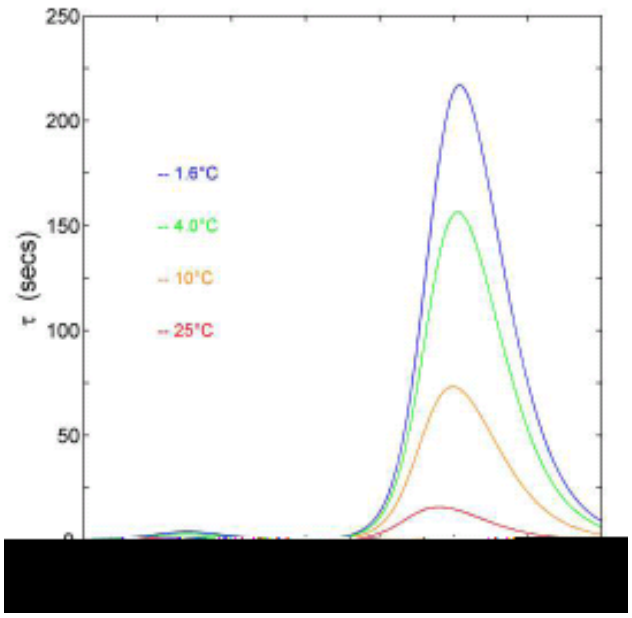


**Figure 5.** The equilibration e-folding time ( ) for a $CO_2$ perturbation of surface sea water as a function of final pH and temperature (Zeebe and Wolf-Gladrow, 2001). For sea water of 25 C and final pH 7.9 a delay line of about 40 seconds would be required to allow time for equilibration before introduction of the enriched fluid to the experimental volume.

For a warm water site such as a tropical coral reef these restrictions do not appear to be impossible. The required sensing, feedback, and flow control systems for executing such experiments are now well underway.

**Figure 6**. A concept drawing for a field $CO_2$ enrichment experiment on a coral flat showing the $CO_2$ source, delivery lines, and circle of emitters. (W. Kirkwood et al., Pers. Com.)