

# **CLIMATE CHANGE AND BIODIVERSITY IN MELANESIA**

**Series editors:  
Stephen J. Leisz and J. Burke Burnett**

## **Biophysical Science - Ocean Acidification**

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**CCBM Paper 2**

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Paper No.	Author	Title
1	Kelvin Richards and Axel Timmermann, IPRC, SOEST, University of Hawaii	Climate change projections for the Southwestern Pacific with a focus on Melanesia
2	Peter G. Brewer, Monterey Bay Aquarium Research Institute	Climate Change and Biodiversity in Melanesia: Biophysical science – ocean acidification
3	Dan A. Polhemus, Department of Natural Sciences, Bishop Museum	Climate change in New Guinea and its potential effects on freshwater ecosystems
4	Geoffrey Hope, The Australian National University	Palaeoecology and resilience in Melanesia: How can palaeoecology contribute to climate change response planning?
5	Steve Coles, Department of Natural Sciences, Bishop Museum	Potential Climate Change Impacts on Corals and Coral Reefs in Melanesia from Bleaching Events and Ocean Acidification
6	Terry J. Donaldson, University of Guam Marine Laboratory	Climate Change and Biodiversity in Melanesia: Implications for and impacts upon reef fishes
7	Rodney V. Salm and Elizabeth Mcleod, The Nature Conservancy	Climate Change Impacts on Ecosystem Resilience and MPA Management in Melanesia
8	Shelley A. James, Department of Natural Sciences, Bishop Museum	Climate Change Impacts on Native Plant Communities in Melanesia
9	Andrew L. Mack, Carnegie Museum of Natural History	Predicting the effects of climate change on Melanesian bird populations: probing the darkness with a broken flashlight



## Synopsis

The lowering of upper ocean pH from the now massive invasion of atmospheric fossil fuel produced CO<sub>2</sub> is an uncontested reality, and is now generally referred to as the process of ocean acidification. We have already disposed of some 530 billion tons of fossil fuel CO<sub>2</sub> by gas exchange with the atmosphere, and the invasion rate today is some 24 million tons per day. This massive removal of CO<sub>2</sub> from the atmosphere is essential for our fossil fuel based economy, and without ocean CO<sub>2</sub> uptake we would already have experienced large-scale climate change. The mean ventilation age of the deep waters of the world ocean (the mean time for re-exposure of the deep waters to the atmosphere) is about 575 years and thus we can count on ocean uptake of CO<sub>2</sub> for some centuries to come. Eventually some 85% of all atmospheric CO<sub>2</sub> emissions will reside in the ocean as air and sea reach equilibrium. This sets limits on allowable accumulated CO<sub>2</sub> emissions if a goal of stabilizing CO<sub>2</sub> levels is set. For example if the atmosphere is held stable at 550 ppmv CO<sub>2</sub> (i.e. doubling of pre-industrial CO<sub>2</sub> level by year 2100, which assumes very rapid carbon emission reduction; cf. IPCC emission scenario B1) for several centuries we will transfer 6.2 trillion tons of CO<sub>2</sub> to the ocean. At that time equilibrium between air and sea will have been achieved, and zero fossil fuel CO<sub>2</sub> emissions to the atmosphere would be allowed. The political acceptability of this ambitious target is unknown.

The transfer of such extraordinary quantities of CO<sub>2</sub> comes at an ecological price, and that price is only now being fully examined and has yet to be fully understood. In pre-industrial times the pH of the surface ocean varied at around 8.2; today the mean value is about 8.1, and if reasonable predictions of CO<sub>2</sub> 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.) require to build their shells. Surface waters today still retain supersaturated levels of aragonite – some have likened this to a “chemical soup” that organisms require to produce their skeletons (Warren, 2007). But this supersaturated horizon is rapidly thinning; this phenomenon is occurring first and most quickly in the high latitude northern and southern oceans. A state of under-saturation is thought to lead to, at minimum, an imbalance in the erosion/accretion rate, or at worst, the outright dissolution of carbonate material, including corals.

But while the first-order chemical changes are known and directly predictable, the impact on marine organisms is far less certain. This is because the ability of animals to adapt to and cope with the stress imposed by higher CO<sub>2</sub> levels and lower pH/carbonate ion concentrations 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<sup>th</sup> century, no record of thinning of these rings from the pH/carbonate ion reduction experienced so far has been reported yet.

While the immediate focus on lowered ocean pH and reduced carbonate ion concentration is understandable, far more complex and widespread issues are quickly emerging. Among these is that the dissolved CO<sub>2</sub> 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<sub>2</sub> from fossil fuels will be the stress of lowered oxygen and higher respiratory CO<sub>2</sub> 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 (HCl) to achieve lowered sea water pH for experiments, rather than the more complex addition of CO<sub>2</sub> itself, can easily create artifacts. Experimental protocols for true field CO<sub>2</sub> enrichment techniques are only now being developed. We know far too little about the response of modern marine animals to the epochal-scale changes in the ocean that are occurring, or the genetic resources possessed by marine animals to cope with such changes; their ability to cope with the combined physiological stresses of temperature, CO<sub>2</sub>, and lowered oxygen levels now being imposed are also still unknown.

## Introduction

Ocean acidification is the lowering of the pH of sea water from the steadily increasing invasion of atmospheric fossil fuel CO<sub>2</sub> by gas exchange across the air-sea boundary.

The basic chemical processes of ocean uptake of CO<sub>2</sub> are relatively straightforward and scientifically well-established. Essentially, carbon dioxide reacts with ocean surface waters to form carbonic acid (H<sub>2</sub>CO<sub>3</sub>) and some is also dissolved as free carbon dioxide (CO<sub>2 (aq)</sub>). The H<sub>2</sub>CO<sub>3</sub> form dissociates, and carbon reassumes in the form of both bicarbonate and carbonate ions. While the ratio of these depends on several factors, the net effect is a reduction in the amount of available carbonate ions. This process also results in, and indeed is measured by, lower pH. As a measure of the concentration of hydrogen ions, a lower pH reflects an increase in the number and activity of hydrogen ions, which can also be stated as an increase in acidity.

Awareness of this issue as a new phenomenon of concern has only recently become widespread in both the public mind and the science community. However, given its likely negative impacts on coralline systems and fisheries such as those throughout Melanesia, it is now 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<sub>2</sub> 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 of atmospheric fossil fuel produced CO<sub>2</sub>.

Geochemical knowledge of oceanic uptake of fossil fuel CO<sub>2</sub> by alkaline sea water has a far longer and impeccable history; it is therefore odd that the biological impacts have been so slowly recognized. Callendar (1938) observed 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”. However, knowledge of ocean mixing rates available at that time assumed a rather rapid ocean uptake (and subsequent sequestration via mixing with deep waters) and therefore a slower and less dangerous 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. Using the power of the newly available <sup>14</sup>C data they estimated that the ocean would take up annually some 40% of CO<sub>2</sub> emissions. Dubbed as a “natural” process, the

oceanic sink was regarded by many as the savior from the atmospheric CO<sub>2</sub>/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<sub>2</sub> emissions. The basic rules for this were established by Sillen (1961), in which the chemistry of the ocean was seen as "the result of a gigantic acid-base titration<sup>1</sup>: acids that have leaked out from the interior of the Earth, HCl, H<sub>2</sub>SO<sub>4</sub>, CO<sub>2</sub>, 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<sub>2</sub> 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 – on the order of hundreds of thousands of years – that carbonate will be replenished by rain water slowly dissolving the granites of the Sierras, the Andes, and other continental mountain ranges that contain oxides of sodium, potassium, etc., and through river discharge to the sea, creating the alkalis that will slowly restore ocean geochemistry. This process is known as silicate rock weathering.

In today's calls for curbing atmospheric CO<sub>2</sub> emissions, the rationale is often given that this will allow time for "natural processes to catch up". That process is predominantly ocean carbon 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, Revelle, and Suess, led them to consider the ocean essentially as a giant well-mixed geochemical box with mixing rates that we now know to be unreasonably fast. The development of more sophisticated approaches, beginning with Oeschger's multi-layered box-diffusion model tuned by the observed <sup>14</sup>C signal (Oeschger et al. 1975) and leading to today's huge and sophisticated global computer models of ocean physical mixing reduced to finer scales, has led to a much more robust understanding of uptake rates. Ocean uptake rates are now estimated at about 30-33% of annual global CO<sub>2</sub> emissions (Sabine et al. 2004). However, the important point is that the underlying insights into the geochemistry of oceanic carbon uptake 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<sub>2</sub> in the ocean is steadily being overwritten by the fossil fuel CO<sub>2</sub> invasion from above. Brewer (1978) first devised a protocol for recovering the fossil fuel CO<sub>2</sub> 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

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<sup>1</sup> i.e. a dynamic process of equilibration between two chemical agents



global survey data the massive fossil fuel CO<sub>2</sub> invasion in great detail (Sabine et al, 2004).

The result is that an accumulation of some 530 billion tons of fossil fuel CO<sub>2</sub> 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.

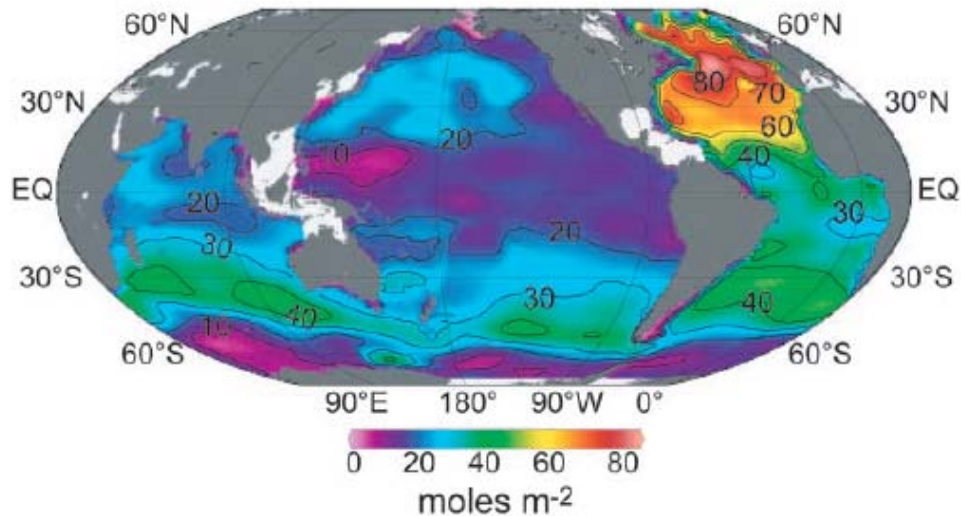


Figure 1. Column inventory of anthropogenic CO<sub>2</sub> in the ocean (mol m<sup>-2</sup>). High inventories are associated with deep water formation in the North Atlantic and intermediate and mode water formation between 30° and 50°S. Total inventory of shaded regions is 106 +/- 17 Pg C. From Sabine 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<sub>2</sub> 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:

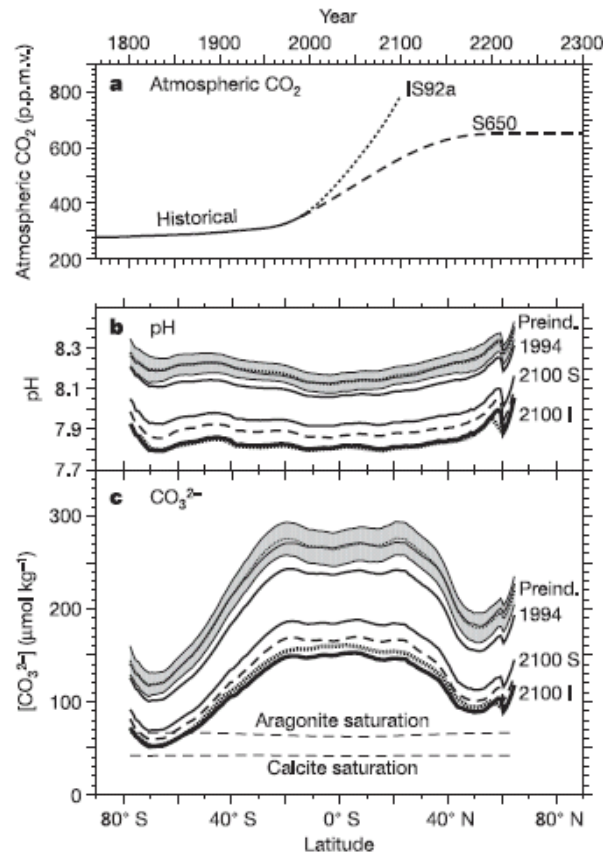


Figure 2. From Orr et al. (2005), showing increasing oceanic surface  $\text{CO}_2$  and decreasing pH over the 21<sup>st</sup> century under two IPCC scenarios for fossil fuel  $\text{CO}_2$  emissions. The resulting change in the saturation state of calcite and aragonite is also shown, indicating actual 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.

Period	$[\text{CO}_2]_{\text{atm}}$ (ppm century <sup>-1</sup> )	Ratio (relative to past 420,000 years)	Temperature (°C century <sup>-1</sup> )	Ratio (relative to past 420,000 years)
Past 420,000 years (99% confidence interval; $n = 282$ )	$0.07 \pm 0.223$	1	$0.01 \pm 0.017$	1
Past 136 years (1870–2006)	73.53	1050	0.7	70
IPCC B1 scenario: 550 ppm at 2100	170	2429	1.8	180
IPCC A2 scenario: 800 ppm at 2100	420	6000	3.4	420

Table 1. From Hoegh-Guldberg et al. (2007). The predicted rate of change of  $\text{CO}_2$  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.

Early experimental work focused on aragonite-based coral ecosystems (Langdon et al., 2002) with the result that a doubling of CO<sub>2</sub> in an experimental ecosystem (Biosphere 2) was found to lead to a reduction in calcification rate of about 40%. 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 a very large literature. Stress on calcifying phytoplankton from mesocosm experiments (Zondervan et al., 2001), on sea urchin development (Kurihara 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<sub>2</sub> levels; the questions are to what degree they are affected, and how effectively animals may be able to compensate for the higher levels. This topic was reviewed in the IPCC Special Report on Carbon Capture and Storage which considered direct deep ocean CO<sub>2</sub> injection as a possible sequestration option (IPCC, 2005). An excellent account is given in recent work by Portner et al. (2004) and Portner (2008), as illustrated in Figure 3.

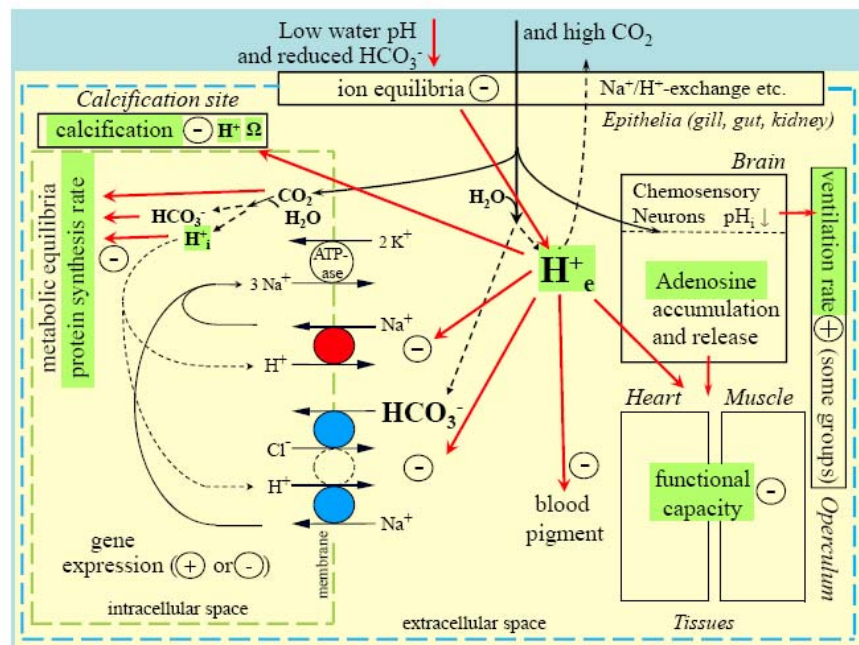


Figure 3. From Portner (2008). Generalized physiological diagram showing the complex of cellular processes involving CO<sub>2</sub> and acid-base functioning in a marine animal.

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<sub>2</sub> and higher CO<sub>2</sub> levels, thus imposing an energy burden, and reducing the resources available for essential functions such as locomotion and reproduction. With rising temperatures, higher pCO<sub>2</sub>, 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<sub>2</sub> will produce an almost equivalent pCO<sub>2</sub> change in surface waters. But when the added mass of CO<sub>2</sub> is carried to deep waters and undergoes the biogenic removal of O<sub>2</sub> and addition of respiratory CO<sub>2</sub>, the chemical change is amplified considerably. A change of +280 ppm pCO<sub>2</sub> (i.e. doubling the pre-industrial value) to surface waters can produce a doubling of pCO<sub>2</sub> at a few hundred meters depth in sub-oxic waters due to the changes in buffer capacity of the fluid – a change for example from 1,000 ppm to 2,000 ppm. The complex interaction of temperature, lowered O<sub>2</sub> and higher pCO<sub>2</sub> 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 thermodynamically will become unable to support marine life.

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<sub>2</sub> levels than are their shallower living counterparts. And for many species the impact of higher CO<sub>2</sub> levels on egg development and larval survival appears to be acute.

The ability of marine animals to cope with thermal stress is reduced under higher dissolved CO<sub>2</sub> 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<sub>2</sub> levels will reduce the zones of the water column that can support life (Portner and Knust, 2007). The combination of warming and anthropogenic CO<sub>2</sub>-induced migrations is thus squeezing habitable marine areas from both north and south.

### **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, CO<sub>2</sub>, and pH 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<sub>2</sub> 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 an atmospheric CO<sub>2</sub> doubling by mid-century and the lowering of ocean pH by 0.4 units by century end; as such it is widely criticized as a pathway to a climate crisis. In fact this intermediate 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; and
- Energy consumed per unit of economic activity will decline to 1/3 of 1990 levels.

The assumptions inherent to IS92a thus pose enormous technical and societal challenges, and we are proceeding far above that path today. In spite of strong public awareness the current CO<sub>2</sub> path (based upon outcomes of the 1990 to 2008 period) appears to be much higher than projections under IS92a. For example global fossil fuel CO<sub>2</sub> emissions grew at 3.3% per year in the period 2000 – 2006, as compared to 1.3% per year in the period 1990 – 1999.

Assuming that IS92a may prove to be an overly optimistic emission scenario, the actual pH and CO<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> solubility and increasing respiration rates. These effects will be large; there is an already observable trend towards decreasing O<sub>2</sub>/higher CO<sub>2</sub> 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<sub>2</sub> waters to night-time surface layers. Thus these large changes in the deeper O<sub>2</sub>/CO<sub>2</sub> 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<sub>2</sub> level studies have yet to be done. More subtle but important is the widespread use of simple acid addition rather than CO<sub>2</sub> 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<sub>2</sub> addition, such as 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<sub>2</sub> enrichment experiments on land the differences can be large. For example experiments on the supposed beneficial effects of higher atmospheric CO<sub>2</sub> 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<sub>2</sub> Enrichment ) Experiments of many kinds (Long et al., 2006; Schimel, 2006). Equivalent *in situ* ocean CO<sub>2</sub> 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, Roberts et al. (2006) have suggested that cold water corals that thrive around the North Atlantic basin are greatly affected by ocean acidification. Yet their close cousins in the Pacific thrive atop sea mounts bathed in sea water that is well under-saturated with respect to aragonite; thus 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<sup>th</sup> century (the <sup>14</sup>C fingerprint from atomic bomb tests, Suess effect showing deposition of anthropogenic CO<sub>2</sub>) no thinning of annual growth rings from the pH changes experienced by the ocean so far have yet been reported.

## Conclusions

- Given the present atmospheric trajectory, future changes in ocean CO<sub>2</sub> status may be underestimated with respect to the rapidity of change, the economic challenge of changing this course, and the additional related impacts of reduced ventilation and increased respiration.
- The combined effects on organisms or ecosystems of higher CO<sub>2</sub>, higher temperature, and lower O<sub>2</sub> 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 but there is evidence that these are the most sensitive life stages of many organisms ranging from corals to fishes (Kikkawa et al., 2003)
- Almost all work has been done at the organismal level, and very little work on the genetic resources that may be available to marine populations to help them adapt to these changes (e.g. latent genes that may be “switched on”) has been carried out.
- Despite *prima facie* evidence that suggests gloomy conclusions, the resilience of ecosystems to adapt to such changes or the co-opting of as yet unknown survival strategies is very much unexplored and yet of critical importance.

## **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<sub>2</sub>-enrichment experiments could very well be considered for sites in Melanesia.

## **Future Research needs**

Many recommendations for research have emerged from the discussion above. These include:

- Longer term studies on full natural systems with true CO<sub>2</sub> 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.
- Detailed data on ocean chemistry, temperature, sea-level, etc., should be gathered at specific sites throughout the Melanesia region to create more robust understanding of environmental changes, and to build regional models that ensure more accurate projections that will inform mitigation/adaptation strategies. Donor organizations to marine protected area projects in the region should make such data-gathering and dissemination part of program grant requirements.

Further research is certainly needed before science can fully and reliably inform the public and policymakers on the likely impact of ocean acidification. In the end, however, the slowing of atmospheric CO<sub>2</sub> emissions is the only practical guard against change. Various proposals to increase ocean alkalinity or pH such as 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.

## **Possible Future Research Models**

In order to carry out field experiments that could reliably predict the future of our high CO<sub>2</sub> levels on the ocean, it is important to look at the FACE (Free Air CO<sub>2</sub> Enrichment) experiments noted above as a potential model. However, it is essential to recognize the fundamental differences between land and ocean CO<sub>2</sub> enrichment techniques. FACE experiments, which are very large scale CO<sub>2</sub> enrichment experiments 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<sub>2</sub> Enrichment (FACE) experiment on forested land in Wisconsin.

Because CO<sub>2</sub> has no atmospheric chemistry, simple mixing of CO<sub>2</sub> with air is all that is required for a land enrichment experiment. But CO<sub>2</sub> 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 ( $\tau$ ) 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<sub>2</sub> to sea water to allow the equilibrium signal to develop – a minimum of  $2\tau$  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<sub>2</sub> enriched fluid.



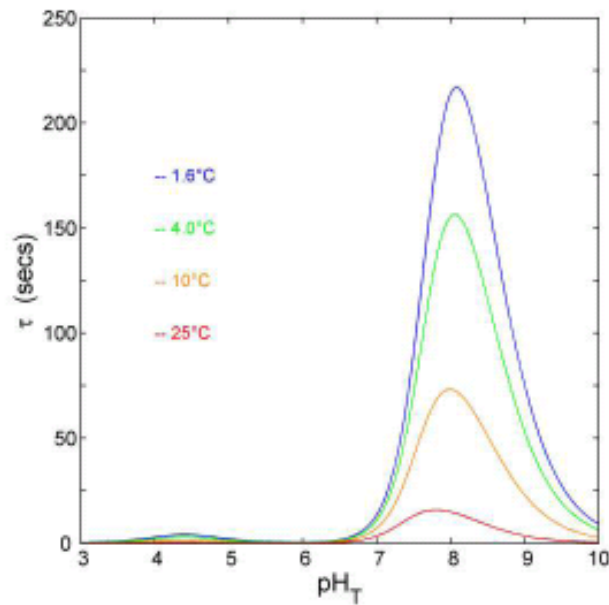


Figure 5. The equilibration e-folding time ( $\tau$ ) for a  $\text{CO}_2$  perturbation of surface sea water as a function of final pH and temperature (Zeebe and Wolf-Gladrow, 2001). For sea water of  $25^\circ\text{C}$  and final pH 7.9 a delay line of about 40 seconds would be required to allow time 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 and Figure 7 sketch out how a Free Ocean  $\text{CO}_2$  Enrichment experiment could be designed and regulated.

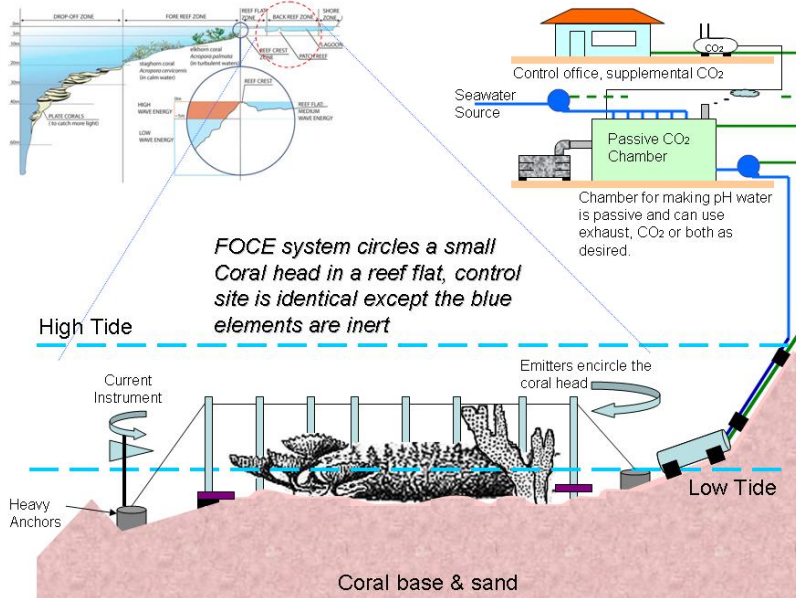


Figure 6. A concept drawing for a field CO<sub>2</sub> enrichment experiment on a coral flat showing the CO<sub>2</sub> source, delivery lines, and circle of emitters. (W. Kirkwood et al., Pers. Com.)

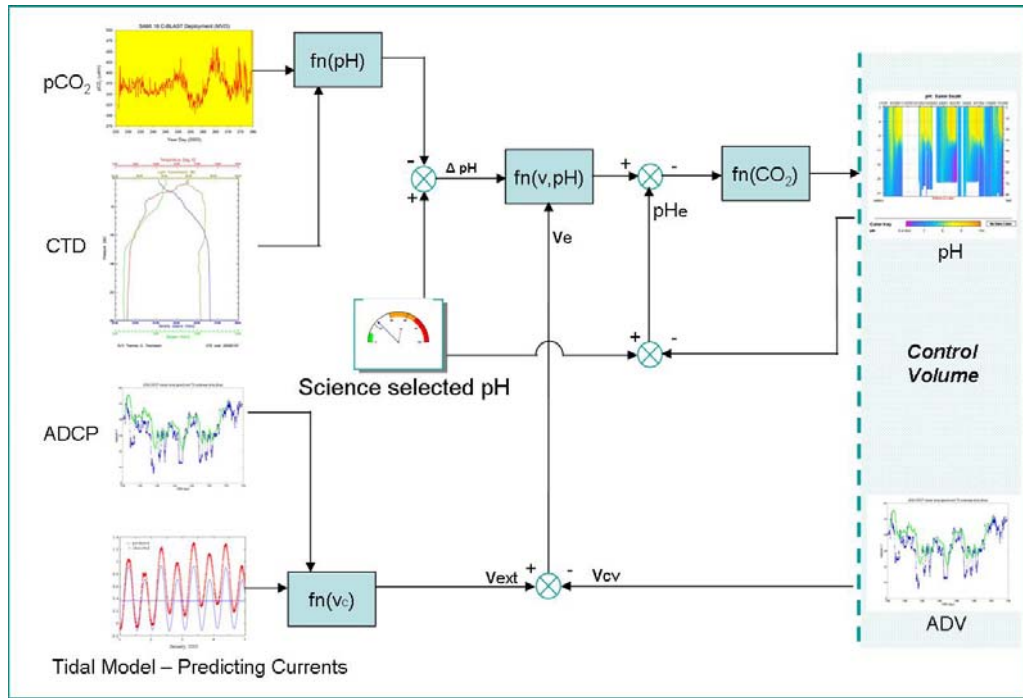


Figure 7. Scheme for feed-back control of CO<sub>2</sub> based on pH sensing and changing velocity for simulating exposure to a future higher CO<sub>2</sub> ocean environment. These functions have already been tested successfully in short-term pilot programs (W. Kirkwood et al., Pers. Com.).

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