# TOWARDS AN INTEGRATED GLOBAL OCEAN ACIDIFICATION OBSERVATION NETWORK

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## ABSTRACT

The increase in atmospheric carbon dioxide ($CO_2$), originating largely from human fossil fuel combustion and deforestation since the beginning of the industrial era, is causing a decrease in ocean pH and changes to seawater carbonate chemistry. This process, termed ocean acidification, is now well established from modeling and field data, and the rate of change in ocean pH and carbon chemistry is expected to increase significantly over this century unless future $CO_2$ emissions are restricted dramatically. The rate of $CO_2$ increase is the fastest the Earth has experienced in 65 million years (Ridgwell and Schmidt, 2010), and the current concentration is estimated to be the highest in, at least, the past 50 million years (Zachos et al., 2008). Central to predicting the atmospheric carbon inventory during the 21st century will be understanding and predicting the adjustments in the ocean uptake and exchange of both anthropogenic and natural $CO_2$. To quantify these changes on a global scale, an international interdisciplinary program of ship-based hydrography, time-series moorings, floats and gliders with carbon, pH and oxygen sensors, and ecological surveys is already underway. This program together with implementations of molecular technology will help scientists determine the extent of the large-scale changes in the carbon chemistry of seawater and the associated biological responses to ocean acidification in both open ocean and coastal environments. Indeed many countries are presently engaged in ocean acidification research and monitoring activities. Some examples include the European Union (EPOCA, EuroSITES, MEECE), German (BIOACID), UK (UK Ocean Acidification Research Programme), US (emerging program supported by NSF, NOAA, NASA, USGS) and Japan (programs supported by MoE and MEXT) ocean acidification research programmes. The proposed activities will require a coordinated international research effort that is closely linked with international carbon research programs, such as the CLIVAR/$CO_2$ Repeat Hydrography (GO-SHIP) Program, the Integrated Ocean Drilling Program, and

the IGBP programmes SOLAS and IMBER. The Global Ocean Acidification Observation Network will interface strongly with the data synthesis, archiving and management activities of existing international ocean acidification programs.

## 1. INTRODUCTION

Human activities from the beginning of industrialization have resulted in an accelerating increase in atmospheric carbon dioxide levels ($CO_2$) from approximately 280 parts per million (ppm) at the end of the 19th century to the current levels of 390 ppm $CO_2$ (2010 levels). During this time, the oceans have absorbed about one-third of the anthropogenic carbon emissions (Sabine et al. 2004), which represents a great advantage to the Earth's biosphere because the ocean uptake of $CO_2$ reduces greenhouse gas levels in the atmosphere, potentially ameliorating global warming. When $CO_2$ dissolves in seawater the concentrations of carbon dioxide ($[CO_2]$) and bicarbonate ($[HCO_3^-]$) increase and both the pH and the concentration of carbonate ions ($[CO_3^{2-}]$) decrease. This process, referred to as ocean acidification (Figure 1) can be accelerated as a result of human activities, and has already decreased the ocean pH by about 0.1 unit since the beginning of industrialization (Caldeira and Wickett, 2003; 2005; Orr et al., 2005), with an annual decline of ~0.0017 units observed over the last quarter century at several open ocean time-series sites (Bates, 2007; Bates and Peters, 2007; Santana-Casiano et al., 2007; Dore et al., 2009). The continuing process of ocean acidification has long been documented (Feely and Chen, 1982; Feely et al., 1984; Feely et al., 1988), and observations reveal an unquestionable direct impact of increases in atmospheric $CO_2$ on the $CO_2$ levels in the surface ocean $p$CO$_2$ as is shown by the surface ocean $p$CO$_2$ following the trend in atmospheric $CO_2$ increase over the past 20 years (Figure 1). While the current levels of $CO_2$ are not unprecedented in the history of Earth, current $CO_2$ levels are thought to be the highest for at least the last 50 million years (Zachos et al., 2008). Additionally, the rate of increase in $CO_2$ is thought to be at least an order of magnitude faster than has occurred for 65 million years (Ridgwell and Schmidt 2010). The rate of increase in dissolved $CO_2$ (and the associated changes in the carbon chemistry of the oceans) will undoubtedly have an impact upon marine life, but whether or how marine biota will acclimate (changes in physiological performance) or adapt (selection of ecotypes through time) to ocean acidification remains an open question. A central concern for calcifying marine animals and plants is that ocean acidification reduces the concentration of $CO_3^{2-}$ in seawater, which is essential for the production of calcium carbonate ($CaCO_3$) biominerals used by organisms to form their plates, skeletons, shells and even entire reef structures. As the carbonate

concentration decreases in the open ocean, the saturation state ($\Omega$) of the two $CaCO_3$ polymorphs, calcite and aragonite, [$\Omega = [Ca^{2+}][CO_3^{2-}] / K'_{sp}$ (where $K'_{sp}$ is the apparent solubility product constant for calcite or aragonite) decreases. It has been suggested that the values for $\Omega$ will decline to <1 (undersaturation) with respect to aragonite around the year 2032 in the Arctic Ocean (Steinacher et al., 2009; Feely et al., 2010), and by around 2050 in the Southern Ocean (Orr et al., 2005) with potential disruptions likely to many components of the marine food web.

In addition to projected changes in $\Omega$ and pH, if atmospheric $CO_2$ concentrations continue to rise, this will lead to significant temperature increases in both the atmosphere and the surface oceans in the coming decades. The combined effects of $CO_2$ and temperature (and other climate-related variables) are mostly unknown, but it has been suggested that their combined impacts could be different from either one on its own (Reynaud et al., 2003; Findlay et al. 2009; Walther et al., 2009). Some unanswered questions include the feedbacks between biota and water chemistry especially in shallow-water systems, the biological acclimation and adaptation to ocean acidification, and the threshold levels for physiological tolerance (tipping points) at the scales from organism to community levels. This additional information is required to help predict the socio-economic impact of ocean acidification and to provide clear evidence on the impacts of acidification to policy makers as they consider timelines and strategies for $CO_2$ emission mitigation.

## 2. SOME FACTS ABOUT OCEAN ACIDIFICATION

Results from the global ocean $CO_2$ surveys over the past two decades demonstrate that ocean acidification is an indisputable consequence of rising atmospheric $CO_2$. Seawater carbonate chemistry is controlled by a series of chemical equilibria, invasion and evasion of $CO_2$ across the air-sea interface, exchange, dissolution and precipitation reactions of $CaCO_3$. Atmospheric $CO_2$ equilibrates with dissolved $CO_2$ in seawater [$CO_{2 \text{ (atmos)}} \Leftrightarrow CO_{2 \text{ (aq)}}$], and any increase in the partial pressure of $CO_2$ in the atmosphere reaches equilibration with the ocean surface water within about a year. $CO_2$ reacts with seawater to form carbonic acid ($H_2CO_3$), a weak acid. A major fraction of the $H_2CO_3$ dissociates into hydrogen ions ($H^+$) and bicarbonate ions ($HCO_3^-$). Some of the $H^+$ reacts with carbonate ions ($CO_3^{2-}$) to produce $HCO_3^-$ ions. As a result, $CO_2$ uptake by the oceans causes an increase in $H^+$, and consequently lowers pH and $CO_3^{2-}$ concentrations:

$$CO_{2 \text{ (aq)}} + H_2O \Leftrightarrow H_2CO_3 \Leftrightarrow H^+ + HCO_3^- \Leftrightarrow 2H^+ + CO_3^{2-}$$
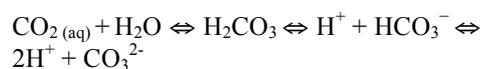
While the $CO_2$ hydration reaction is relatively slow, the reactions between $H^+$ and $HCO_3^-$ and $CO_3^{2-}$ are extremely fast. The formation of $H_2CO_3$ occurs within 10s of seconds and the interconversion of $HCO_3^-$ and $CO_3^{2-}$ takes place within microseconds. For surface open ocean conditions, about 90% of the total carbon is in the form of the bicarbonate anion ($HCO_3^-$), ~9% as carbonate ($CO_3^{2-}$), and ~1% remains as $CO_{2(aq)}$ and $H_2CO_3$.
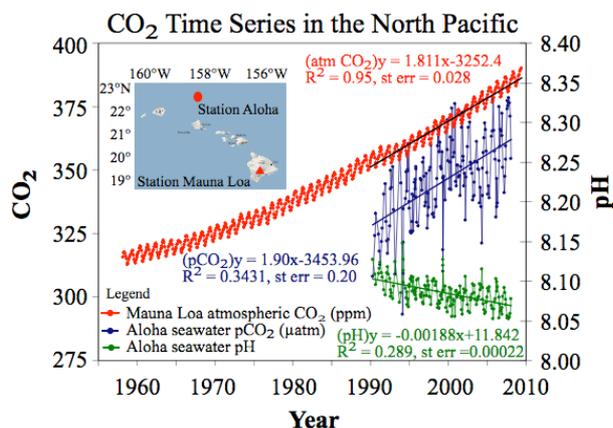


***Figure 1***: *Time series of atmospheric $CO_2$ at Mauna Loa (in parts per million, ppm) and surface ocean pH and $pCO_2$ (µatm) at Ocean Station Aloha in the subtropical North Pacific Ocean. Note that the increase in oceanic $CO_2$ over the last 17 years is consistent with the atmospheric increase within the statistical limits oft he measurements. Mauna Loa data: Dr. Pieter Tans, NOAA/ESRL (http://www.esrl.noaa.gov/gmd/ccgg/trends); HOT/Aloha data: Dr. David Karl, University of Hawaii (http://hahana.soest.hawaii.edu) (modified after Feely, 2008).*

Another process that impacts upon the equilibria of the carbonate species is calcification: $Ca^{2+} + CO_3^{2-} \Leftrightarrow CaCO_{3(s)}$. The saturation state ($\Omega$) affects the extent of biologically-mediated calcification although the exact relationship between carbonate precipitation and $\Omega$ remains unclear. The term $\Omega$ differs for different mineral forms of the precipitating carbonate (e.g. aragonite and calcite) as well as the Mg content (Feely et al., 2004; Morse et al., 2006; Lebrato et al., 2010). Many of the marine organisms producing skeletons or body parts of solid-phase $CaCO_3$ are known to be sensitive to the concentration of $CO_3^{2-}$ in seawater (e.g. Kleypas et al., 2006). Although most surface waters in the global ocean are currently supersaturated with respect to aragonite and calcite ($\Omega > 1$), a decrease in current values will affect organisms with optimal carbonate precipitation rates above these saturation states. For example, a lowering of $\Omega$ for aragonite from 4 to 3 is predicted to lead to significant reduction in calcification rates of tropical reef corals (Kleypas et al., 1999; Silverman et al., 2009).

Three biotic processes affect the direction of $CO_2$ fluxes between the upper ocean and the atmosphere: photosynthesis utilizes $CO_2$ at the surface and thus increases the seawater pH while respiration releases $CO_2$ in the surface ocean and throughout the water column: $CO_2 + H_2O \Leftrightarrow$ "$CH_2O$" $+ O_2$. Calcification uses $CO_3^{2-}$ and $HCO_3^-$ but since $HCO_3^-$ concentration in seawater is more than an order of magnitude greater than that of $CO_3^{2-}$ in seawater, it is thought that most calcifiers are able to utilize $HCO_3^-$. Bicarbonate utilization in the calcification process produces $CO_2$ as a byproduct: $2HCO_3^- + Ca^{2+} \Leftrightarrow CaCO_3 + CO_2 + H_2O$ [only about 0.6 moles of $CO_2$ are released for each mole of $CaCO_3$ precipitated (Frankignoulle et al., 1994)]. Photosynthesis also produces a large fraction of the annual global supply of oxygen (and consumes nutrients such as nitrate, phosphate, silicate, and iron, all of which can be limiting in different parts of the ocean). Further, the downward flux of organic matter from the ocean surface to the deep sea is re-oxidized by respiration back to $CO_2$, thereby sequestering $CO_2$ from the atmosphere but also acidifying the deep sea. The use of oxygen in this process and additional loss of oxygen from the surface oceans caused by warming (Keeling et al., 2010) could have severe effects on marine biota, particularly those populating future expanded oxygen minimum zones (Gruber and Körtzinger, 2010). Additionally, ocean acidification-driven changes in phytoplankton physiology may have an effect on nutrient (e.g., N, P, C) utilization and oxygen consumption. Although the focus of global carbon monitoring programs is on measuring $CO_2$, oxygen measurements are required particularly when investigating the effect of ocean acidification on biologically-relevant processes involving the cycling of $CO_2$ and $O_2$. For example, the most abundant protein on Earth, RuBisCO (ribulose-1,5-bisphosphate carboxylase oxygenase) catalyses either the carboxylation or the oxygenation of ribulose-1,5-bisphosphate with $CO_2$ or $O_2$. Therefore, monitoring not only $CO_2$ but also $O_2$ and changes in the availability of nutrients is key to understanding the effect of processes like ocean acidification on biological activities of biogeochemical relevance (Doney, 2010).

## 3.    NATURAL FLUCTUATIONS IN pH

The effects of ocean acidification on the chemistry of ocean waters are well verified from models, open-ocean hydrographic surveys, and time series data (Bates, 2007; Bates and Peters, 2007; Caldeira and Wickett, 2003; Caldeira and Wickett, 2005; Chung et al., 2003; Feely et al., 2008; Feely et al., 2002; Feely et al., 2004; Orr et al., 2005; Sabine and Feely, 2007; Santana-Casiano et al., 2007; Dore et al., 2009;

Olafsson et al., 2009). Data generated from these efforts have established a background of temporal and spatial variability in carbonate chemistry (e.g., Watson, et al., 2009) that provides a framework within which to study causes and effects of ocean acidification. At the Hawaii Ocean Time-Series (HOT) station ALOHA the observed increases in surface water $p$CO$_2$ and atmospheric CO$_2$ agree well (Figure 1), and further indicate that the uptake of anthropogenic CO$_2$ is the major cause for long-term increases in dissolved inorganic carbon (DIC) and decreases in CaCO$_3$ saturation state (Doney et al., 2009; Dore et al., 2009). Decadal time-scale pH reductions are also observed in a south-to-north basin-scale transect in the North Pacific (Byrne et al., 2010a). However, while ocean acidification is a global-scale phenomenon, there are areas that already have naturally low pH conditions; e.g., modeling studies have suggested that the high latitude oceans (Arctic and Southern Oceans) will experience aragonite undersaturation by the middle of this century (Cao and Caldeira, 2008; Gehlen et al., 2007; Orr et al., 2005; Feely et al., 2009). Also, Steinacher et al. (2009) argue that the surface Arctic Ocean will start experiencing localized aragonite undersaturation within the next decade. Shoaling of undersaturated waters has been observed in the North Pacific (Feely et al., 1982; 1984; 1988; 2004), and the Chukchi Sea and the Arctic Ocean (Bates et al., 2009; Yamamoto-Kawai et al., 2009).

Feely et al. (2008) presented evidence to show that the continental shelf of the west coast of North America may already be experiencing seasonally undersaturated conditions for aragonite, resulting from the combined impacts of coastal upwelling and ocean acidification (Figure 2). Here the seasonal upwelling along the coast brings CO$_2$-enriched waters up into the near-bottom waters and, in some instances, all the way to the surface ocean. There is evidence from increasing extent of low-oxygen waters on the shelf that either the source waters and/or the strength of upwelling are changing in this region (Feely et al., 2008). The evidence suggests that this water, in addition to its original high level of CO$_2$ resulting from natural respiration processes in the subsurface layers, is also enriched with anthropogenic CO$_2$ from gas exchange and vertical mixing. The CO$_2$ concentration in these upwelled waters is therefore now greater than it would have been in pre-industrial times. Also, these "acidified" upwelled waters are undersaturated with respect to aragonite, which may be a potential threat to many of the calcifying aragonitic species that live in these coastal regions. Seasonal upwelling is a common phenomenon in many coastal regions, and thus this process may be affecting coastal ecosystems in other locations as well.
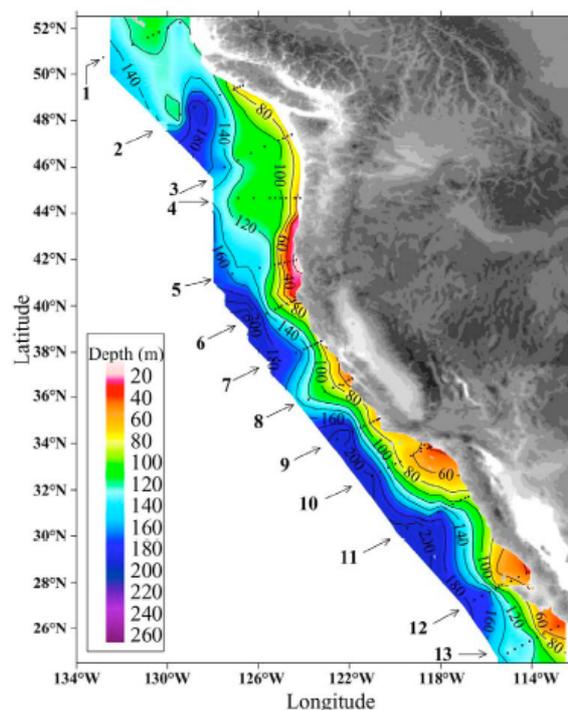


***Figure 2.*** *Distribution of the depths of the undersaturated water (aragonite saturation < 1.0; pH < 7.75) on the continental shelf of western North America from Queen Charlotte Sound, Canada to San Gregorio Baja California Sur, Mexico. On transect lines 5 the corrosive water reaches all the way to the surface in the inshore waters near the coast. The black dots represent station locations (Feely et al., 2008).*

## 4. ADAPTATION OF MARINE BIOTA TO OCEAN ACIDIFICATION

By the end of this century atmospheric carbon dioxide levels could reach more than 800 ppm (IPCC AR4), which means that, by 2100, the hydrogen ion concentration of the ocean surface would have increased by about 150% relative to the beginning of the industrial revolution. The big question facing biologists is whether, and to what extent, marine animals and plants will be able to acclimate or adapt to the fast rate of pH change.

Photosynthetic carbon fixation by primary producers including diatoms (Tortell et al., 2000; 2008) and coccolithophores (Riebesell et al., 2000; Iglesias-Rodriguez et al., 2008; Shi et al., 2009) seems to be, in most cases, either unaffected or enhanced by ocean acidification. However, as CO$_2$ levels increase in seawater, those species that have evolved mechanisms to acquire inorganic carbon under low CO$_2$ (CO$_2$-

| Physiological Response / Major group | # species studied | Response to increasing $CO_2$ a | b | c | d | References |
|---|---|---|---|---|---|---|
| **Calcification** | | | | | | |
| Coccolithophores | 5 | 9 | 3 | 3 | 3 | 11,34,35,44,55,61,118,128,162/57,83,14057,118,12e5,1245,104,105 |
| Planktonic Foraminifera | 2 | 3 | - | - | - | 12,13,145/-/-/- |
| Molluscs | 6 | 5 | - | - | - | 64,67,76,118,121/-/-/- |
| Echinoderms | 3 | 3 | 3 | - | - | 27,43,11466,157/-/131 |
| Corals | 12 | 11 | - | - | 1 | 7,32,43,72,73,86,89,94,101,102,107/-/132/- |
| Coralline red algae | 1 | 1 | - | - | - | 98/-/-/131 |
| Arthropods | 2 | 2 | 1 | - | - | 3,109/131/-/- |
| **Photosynthesis** [1] | | | | | | |
| Coccolithophores [2] | 2 | 1 | 5 | - | 1 | 57/5,57,83,128,140/57/- |
| Prokaryotes | 2 | - | 2 | 1 | - | -/59,80/59/- |
| Seagrasses | 5 | - | 4 | - | - | -/85,123,142,161/-/- |
| Diatoms | * | - | 2 | - | - | -/148,150/-/- |
| **Nitrogen Fixation** | | | | | | |
| Cyanobacteria | 2 | 1 | 5 | - | - | 33/4,59,80,97,109/-/- |
| **Reproduction, development, metabolic health** | | | | | | |
| Molluscs | 2 | 5 | - | - | 1 | 1,37,76,113,124/-/78/- |
| Echinoderms | | 3 | - | - | - | 6,43,99/-/-/- |
| Arthropods | 1 | 3 | - | - | 1 | 112,154,158/-/3/- |

***Figure 3***. *Responses of some groups of marine organisms to ocean acidification. The response curves on the right indicate four cases: (a) linear negative, (b) linear positive, (c) level, and (d) non-linear parabolic responses to increasing levels of seawater partial pressure of $CO_2$ for each of the groups (from Doney et al., 2009). * indicates natural assemblages.*

concentrating mechanisms) may be outnumbered by those relying largely on $CO_2$. In seagrasses, growth and light-saturated photosynthetic rates are also increased under high $CO_2$ conditions (Palacios and Zimmerman, 2007; Zimmerman et al., 1997) but decreased in calcifying macroalgae (Gao and Zheng, 2010). Field manipulations revealed that the combined effect of temperature and $CO_2$ appeared to control phytoplankton population composition (Tortell et al., 2008). Also, some coral species in mesocosm experiments show enhanced productivity under $CO_2$ up to 560 ppm, but severely reduced productivity under $CO_2$ regimes approaching 1000 ppm (Anthony et al. 2008). Ocean acidification has been found to cause a decline in Fe availability to phytoplankton (Shi et al., 2010) and pH-induced shifts in nutrient stoichiometry have been found to influence community structure, ratio of nutrient (Si:N:P) utilization and productivity (Tortell et al., 2002; Blackford, 2010). Nitrogen-fixation appears to be enhanced by elevated $CO_2$ in *Trichodesmium* sp. (Barcelos e Ramos et al., 2007; Hutchins et al., 2007) (Figure 3). Marine calcification seems to decline with decreasing carbonate ions, although there is some variability in the magnitude and direction of the slope (e.g., Lindinger et al., 1984; Spicer, 1995; Spero et al., 1997; Gattuso et al., 1998; Bijma et al., 1999; Harris et al., 1999; Kleypas et al., 1999; Langdon et al., 2000; Riebesell et al., 2000; Kleypas et al., 2001; Zondervan et al., 2001; Bates, 2002; Bijma et al., 2002; Feely et al., 2002; Leclercq et al., 2002; Zondervan et al., 2002; Guinotte et al., 2003; Langdon et al., 2003; Reynaud et al., 2003; Green et al., 2004; Jones et al., 2004; Kurihara et al., 2004; Delille et al., 2005; Engel et al., 2005; Kayane et al., 2005; Langdon and Atkinson, 2005; Langdon and

Atkinson, 2005; Orr et al., 2005; Guinotte et al., 2006; Kleypas et al., 2006; Langer et al., 2006; Langer et al., 2009; Gazeau et al., 2007; Miles et al., 2007; Cooper et al., 2008; Dupont et al., 2008; Fabry et al., 2008; Feng et al., 2008; Hall-Spencer et al., 2008; Iglesias-Rodriguez et al., 2008; Kuffner et al., 2008; Wood et al., 2008; Arnold et al., 2009; Clark et al., 2009; Gao et al., 2009; Gooding et al., 2009; Ries et al., 2009; Shi et al., 2009; Wood et al., 2008; Barcelos e Ramos et al., 2010; Bierman and Engel, 2010; Comeau et al., 2010; De Bodt et al., 2010; Fiorini et al., 2010; Müller et al., 2010; Nienhuis et al., 2010; Rickaby et al., 2010; Rodolfo-Metalpa et al., 2010). However, the calcification response to ocean acidification remains unresolved in coccolithophores where significant variation has been observed between and even within species (Riebesell et al., 2000; Zondervan et al., 2001; Zondervan et al., 2002; Langer et al., 2006; Fabry et al., 2008; Iglesias-Rodriguez et al., 2008; Shi et al., 2009; Fiorini et al., 2010, Langer et al., 2009; Müller et al., 2010).

The observed inter- and intra-specific diversity in the responses to ocean acidification in coccolithophores may be the result of genetic variants (Riebesell et al., 2009) conferring distinct adaptations to pH and carbon utilization, enabling efficient utilization of $CO_3^{2-}$ from $HCO_3^-$ acquisition, for example. Evolutionary adaptation via intraspecific genetic diversity has been argued to be the case in coccolithophores (Iglesias-Rodriguez et al., 2002, 2006), which show a broad range of calcification responses within the species concept (Langer et al., 2009; Fabry et al., 2008). Increased $CO_2$ and its consequent changes in ocean chemistry may alter not only the physiology of organisms but also benthic community dynamics, species composition and patterns of succession. Since the sum of the molar concentration of all forms of DIC in seawater ($<2.5$ mmol $kg^{-1}$) is less than one-quarter the molar concentration of $Ca^{2+}$ in seawater ($\sim10.2$ mmol $kg^{-1}$), carbonate ions are likely the limiting substrate in marine calcification (Langdon and Atkinson, 2005). And since the average concentration of $CO_3^{2-}$ in open ocean surface seawater ($\sim0.19$ mmol $kg^{-1}$) is approximately one order of magnitude smaller than concentration of $HCO_3^-$ in seawater ($\sim1.9$ mmol $kg^{-1}$), it is perhaps expected that the ability to utilize $HCO_3^-$ in calcification would have been selected for in the evolution of calcifying marine organisms. Thus, although ocean acidification is expected to have profound impacts on marine biogeochemical and biological processes in the coming decades, selective pressures for alternate mechanisms of calcification will increase. In addition to ocean acidification, predicted increases in temperature will undoubtedly impact upon metabolic rates and organism health. For example, a decline in coral reef accretion rates, due to simultaneous increases in temperature and decreases in

carbonate ion concentration (Silverman et al., 2009), would have negative impacts on fish and invertebrate assemblages that rely on corals for habitats (e.g. Jones et al., 2004), coastal protection, and food webs. The increase in $p$CO$_2$ can also impact on the physiology of marine biota through acid-base imbalance and reduced oxygen transport capacity (Fabry et al., 2008; Rosa and Seibel, 2008). The extent to which an organism will adapt to selection pressure depends upon its genetic make up such that groups with active proton pumps, mechanisms for active uptake of bicarbonate and conversion into carbonate when carbonate ions are scarce, will have an advantage with respect to organisms that rely on carbonate availability. The question remains what ecological and societal consequences will arise from any loss of functional groups, and how the new dominant groups will impact upon ecosystems, biogeochemical cycles and food availability to humans. The Global Ocean Acidification Observation Network provides a natural laboratory where changes in biological structure, function and biogeochemistry can be measured over time and generate hypotheses testable in experimental settings.

## 5. SOCIETAL EFFECTS OF OCEAN ACIDIFICATION

Losses of calcifying taxa, changes in the trophic interactions and in ecosystem services have been proposed as potential consequences of ocean acidification (Cooley et al., 2009). For example, a change in calcification rates in molluscs, corals, echinoderms or coccolithophores as concentrations of CO3- decrease (Kleypas et al., 2006; Doney et al., 2009; Turley et al., 2010), or in photosynthesis and nitrogen fixation as concentrations of CO2 and HCO3- increase (Tortell et al., 2000; Hutchins et al., 2007) could affect the yield of food harvest, elemental fluxes and ultimately humankind's income. Although the impact of ocean acidification on food supply is presently difficult to predict with certainty, given that fisheries provide up to 20% of protein in Southeast Asian countries, western coastal Africa and western and northern Europe (http://faostat.fao.org; Cooley et al., 2009), elucidating the impacts of ocean acidification on the yield of marine products is a priority. Although organism-level responses are still poorly understood (Fabry et al., 2008; Doney et al., 2009), some negative effects of ocean acidification on reproduction and development have been suggested for some commercially important animals (Kurihara and Shirayama, 2004; Gazeau et al., 2007; Dupont et al., 2008). However, there is some variability in the response of some species with planktonic larvae, such as crabs, lobster, and shrimps (Arnold et al., 2009; Ries et al., 2009; Walther et al., 2009). Apparently early-history stages of a range of invertebrates including krill are highly sensitive to ocean acidification (Kurihara et al., 2004). It is also known that some adaptations in physiological performance come at a metabolic cost, for example in echinoderms (Wood et al., 2008). The uncertainties in whether and how marine biota will acclimate or adapt to the rate of change in ocean carbon chemistry affect our ability to predict economic impacts (Cooley and Doney, 2009). These uncertainties will be reduced at least in part with global data from Global Ocean Acidification Observation Network time series and experimental manipulations in locations of distinct carbonate chemistry characteristics harboring different functional groups species.

## 6. MONITORING CO$_2$ ON DECADAL TIME SCALES

Measurements of the CO$_2$ system in surface waters started more than half century ago (Keeling, 1965). Over the last several decades, questions concerning biogeochemical effects of climate change have focused on developing a framework to measure the link between potential biological acclimation, population physiology, biogeochemical cycles and climate change. The extent to which these relationships can be assessed is critically dependent upon the ability to combine laboratory experiments and field observations testing biological adaptation (selection of organisms/groups under environmental selection pressure) and biogeochemistry in 'real time', combining physiological techniques, emerging molecular technology, and robust measurements of pH and carbonate chemistry.

For this purpose, the vision of the OceanObs community is to use emerging platforms and technology to test the effect of ocean acidification on the evolution/adaptation capability as well as acclimation of marine biota and their biogeochemical repercussions. This vision involves time series measurements in open ocean and coastal observatories, experiments and autonomous measurements aboard voluntary observing ships (VOS), mesocosm experiments, global and regional monitoring using satellite data, and cooperation with Integrated Ocean Drilling Program (IODP) operations. An overarching objective is the formation of a global network with good spatial and temporal coverage (see Gruber and Körtzinger, 2010) to infer past changes and calibrating short and long term chemical and biological effects of ocean acidification.

A strategy combining regional and global networks of observations and process studies, and manipulative experiments involving a suite of organisms in laboratory experiments, mesocosm and field studies, technological advances, and new modelling approaches are required to fulfil this vision. Parameters that can be measured routinely onboard ships include temperature, salinity, oxygen, nutrients, $p$CO$_2$, pH, total alkalinity

(TA), DIC, dissolved organic carbon (DOC) and particulate organic and inorganic carbon (POC, PIC). While some of these chemical parameters (e.g., $pCO_2$ and pH) can be measured on moorings, autonomous sensors are not yet broadly utilized on a global scale. Moreover, new method development is required for routine measurements of DIC and TA and proxies that may indicate stress on biological organisms. This paper provides a strategy for a global ocean acidification observing system in the major ocean basins and marginal seas, including environments harbouring warm and coldwater corals, coastal margins, tropical to subtropical open-ocean regions, and high-latitude regions.

### 6.1. Objectives of a Global Ocean Acidification Observation Network

- To establish an international effort to coordinate global sampling and analysis of pH and carbonate chemistry following The Guide to Best Practices in Ocean Acidification Research and Data Reporting (Riebesell et al., 2010).

- To improve current representations, predictions and hindcasting of ocean pH and carbonate chemistry in the context of ocean acidification.

- To assess the combined effects of ocean acidification with other climate-relevant processes (e.g., temperature increases, nutrients and oxygen depletion).

- To assess the effect of seasonal and interannual pH and carbonate chemistry fluctuations on biotic interactions, physiological performance and biogeochemical impacts.

- To provide the scientific and extended community with measured data to analyse trends in ocean pH and carbonate chemistry over time and assess the potential effect on goods and services provided by the oceans, including food supply.

- To provide sound scientific evidence on current and future ocean acidification and its consequences to policy and decision makers, marine resource managers and society as a whole.

### 6.2. Implementing ocean acidification best practices

Implementing best practices for ocean acidification research is now identified as a priority by the ocean acidification community. Programs such as OOI, IOCCP, and the SOLAS/IMBER ocean acidification working group can make a difference in the extent of spatial and temporal 'mapping' of changes in global ocean pH and carbonate chemistry. Bringing together different disciplines, levels of organization (from molecular to global) and establishing a network for data analysis and synthesis, the Global Ocean Acidification Observation Network will transform our

scientific knowledge providing near real-time information on the extent and rate of ocean acidification and its biological consequences. Continuous data flow from sensors and computing networks will provide information on vulnerable areas where more detailed experiments can be carried out. For example, platforms operating at high latitudes are primary candidates for experiments to test the effect of naturally $CO_2$-rich and lower carbonate saturation seawaters on population physiology and biogeochemical properties.

### 6.3. Short- and long- term synergistic effects of ocean acidification and other climate-relevant variables

Assessing long-term trends in ocean pH requires coordination between surface ocean measurements on VOS, established ocean observatory sites both in open and coastal sites, on moorings and float/glider-based observatories, and with satellite-derived information. This has been a central role of the ship-based global $CO_2$ survey conducted by WOCE-JGOFS programs in the 1990s which resulted in novel high quality data sets with global coverage (Wallace, 2001; Sabine et al., 2004). Since then, GLODAP has provided unified global synthesis data on naturally occurring and anthropogenically induced $CO_2$ (Key et al., 2004). Although these data sets are invaluable, two aspects that are missing in the current observation networks are (1) the synergistic effects of climate relevant variables other than ocean acidification; and (2) the impact on the success and physiological performance of marine biota, which are the main drivers of biogeochemical processes. Temperature increases and the expected decline in subsurface oxygen are central to metabolic processes of biogeochemical importance. For example, temperature drives all catalytic processes, controls development in larval stages of animals and causes stress when kinetic thresholds are exceeded. Oxygen declines are predicted due to both solubility effects of increased temperature and altered ocean circulation (Garcia et al., 2005; Brierley and Kingsford, 2009; Keeling et al., 2010) ($O_2$ solubility declines 6% for a 1°C increase in temperature). Ocean deoxygenation will likely have an effect on respiration rates of marine animals and plants and on developmental processes. Also changes in the $O_2$:$CO_2$ ratios are likely to impact upon the oxygenation:carboxylation activity of enzymes such as Rubisco. Therefore, strong coordination with other observation developments for ocean biogeochemistry are required (e.g., Gruber and Körtzinger, 2010). Oxygen is a candidate for inclusion in the measured parameters of the Argo float program (Claustre et al., 2010, Gruber and Körtzinger, 2010) Additionally, working together with the IODP community will provide the temporal dimension that is currently limiting our assessment of long term trends in $CO_2$, $O_2$ and other climate relevant variables and the

impact on community composition over geological time scales. For example, cross calibration using field data, sediment information and laboratory results will be useful in assessing impacts over long time scales. Locations of high sedimentation rates could provide valuable information on high temporal resolution changes in the geological record during the Anthropocene (e.g., Iglesias-Rodriguez et al., 2008; Jonkers et al., 2010). The new WHOI long-corer can be used in assessing changes during glacial/interglacial transitions in platforms such as IODP. The IODP sites could also provide stable platforms to conduct manipulation experiments with natural populations in conjunction with analysis of their record in the sediment.

## 7. OPERATION OF A GLOBAL OCEAN ACIDIFICATION OBSERVATION NETWORK

### 7.1. Community and societal requirements

Our present understanding of the long-term changes in the carbonate system comes from repeat hydrographic sections and time series measurements (Sabine et al 2004; Bates, 2007; Feely et al., 2008; Feely et al., 2004). These studies have played a major role in alerting the scientific and policy making communities of the extent and potential consequences of ocean acidification on a global scale. However, impacts will be felt locally so expanding the global time-series network and the emerging OOI, IOOS, GOOS, OceanSITES with new carbon and pH sensors will provide important information for the scientific community on the changing conditions in open-ocean and coastal environments that are currently undersampled. At present, most of the existing moored carbon observatories only accommodate measurements of $p\mathrm{CO}_2$, which by itself is insufficient to fully constrain the carbon system adequately for effective monitoring and forecasting of ocean acidification and to enable assessment of the parallel biological effects. Ideally, this network would also have the capability to generate data on $\mathrm{CaCO}_3$ saturation states and rates of $\mathrm{CaCO}_3$ production and dissolution. Sensors for DIC and TA are desirable for detecting changes in the marine inorganic carbon system and deposition of other non-$\mathrm{CO}_2$ sources of acidification, particularly in coastal regions (Doney et al., 2007; Ilyina et al., 2009). An increase in upper ocean stratification predicted for this century will lead to a reduced uptake of anthropogenic $\mathrm{CO}_2$ and reduced transport of oxygen from the ocean surface to its interior (Gruber and Körtzinger, 2010). Monitoring of circulation parameters and seawater chemistry and measurements of net community production, either directly or from nutrient or oxygen inventories along with hydrodynamic considerations in coastal zones, are also important for identifying and interpreting biogeochemical and biological responses to ocean acidification. These additional measurements
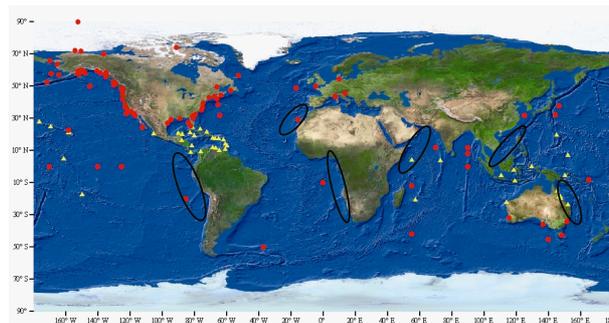


**Figure 4**. *Potential ocean acidification monitoring sites in open-ocean and coastal regions, and potential coral reef ocean acidification monitoring sites. The station locations are given in Feely et al., 2010. Red circles represent deployed or planned open-ocean monitoring sites; yellow triangles represent deployed or planned coral reef monitoring sites. Future sites likely to experience aragonite undersaturation in the near future are indicated by ovals. The entire Arctic Ocean and Southern Ocean are also likely to experience aragonite undersaturation in the near future*

are needed to predict ecosystem responses to ocean acidification. Leveraging existing infrastructure and monitoring programs will enable research to be conducted efficiently and quickly. For example, additional inorganic carbon system measurements and process studies could be conducted at the OceanSITES time series stations (Figure 4) and in areas particularly susceptible to ocean acidification such as the Long-Term Ecological Research in the California Current, Palmer West Peninsula Antarctica and at Moorea. Additional time series stations, repeat surveys, intensified process studies are also required in areas that may be impacted by ocean acidification earliest e.g. Arctic ocean, deep sea, upwelling regions and those of particular socio-economic importance e.g. tropical coral reefs, shelf seas and coastal waters around large estuaries (Turley et al., 2010). Additional time series and repeat surveys in open-ocean and coastal regions are required in order to understand the ocean wide and local changes. Specifically, the community needs the following information at a wide range of localities:

- Time series of carbonate chemistry and seasonal variability through sampling programs. In addition to carbonate chemistry and the usual measured physico-chemical variables (e.g., temperature, salinity, nutrients) simultaneous oxygen measurements are required.

- Changes in the population and community structure with time and changes in the functional properties of the ecosystem. This will be achieved by investigating changes in physiological

performance using a combination of direct measurements of:

o population composition via satellite, video, single cell optical detection of taxon (e.g., fluorescent *in-situ* hybridization for detection of taxa, side scatter for assessment of changes in calcification in populations of coccolithophores);

o production rates including calcification, silicification, nitrogen fixation, photosynthesis using direct measurements in combination with satellite-derived calculations;

o measurements of genetic variables using molecular techniques, for example of changes in gene frequencies, genetic diversity, gene expression, protein expression.

**7.2.** Monitoring real time rate of change in pH and its effects on biology and biogeochemistry

Feely et al. (2010) provide a detailed description of the requirements of a Global Ocean Acidification Observation Network that is fully integrated with the global carbon observing system (Gruber et al., 2010). A coordinated multidisciplinary approach to observations, laboratory and field process studies and modelling is key to achieving a successful research strategy for ocean acidification. This will facilitate the development of our capability to represent and predict future responses of marine biota, ecosystem processes, and biogeochemistry (Fabry et al., 2008). Experiments to date have been largely laboratory-based, which are ideal to establish the physiological processes underlying acclimation in individual species. A small number of studies have conducted $CO_2$ manipulations in mesocosm, ship-board and field experiments, which address the biological complexity in the response of interacting communities. However, all the manipulation experiments have been conducted on time scales that do not address long-term adaptation in the open ocean, and the modification of the carbonate chemistry is generally abrupt, i.e., organisms are exposed to the new condition in one single step or in some incremental pulses that do not represent natural changes. Therefore, while these experimental approaches can provide valuable information on the physiological mechanisms of adaptation to ocean acidification in areas of abrupt pH changes such as upwelling zones, assessing the long-term adaptation in the open ocean and the susceptibility of marine biota to ocean acidification is insufficient with this approach (Boyd et al., 2008). Given that abrupt exposures to corrosive waters occur seasonally (Feely et al., 2008) upwelling events may be useful natural sites to test acclimation and adaptation to abrupt changes in

carbonate chemistry. Submarine volcanic $CO_2$ vents also provide key opportunities to investigate adaptation of benthic organisms and communities (Hall-Spencer et al., 2008). Building an ocean observation network targeting both coastal and open ocean regions of different susceptibilities to ocean acidification will assess the extent of changes in water chemistry over time and will measure impacts at several levels of organization – from chemical to biological. This approach will also take account of the biological complexity and any changes at the population and community levels. It will also measure the effect of any changes in functional group dominance and its biogeochemical impact, and will provide an early warning system for increased vulnerability of habitats to advice on potential time for mitigation or adaptation action.

**7.3.** Existing and emerging technology

In addition to the network of sensors measuring physical parameters including salinity, temperature, photosynthetic active radiation, ultraviolet radiation, pressure, acoustic Doppler current profiler, a number of chemical sensors are already part of the ecosystem observation network. Sensors of pH or fugacity of $CO_2$ ($f$$CO_2$) combined with sensors for total alkalinity or DIC are the best approach to characterize the carbonate system (Byrne et al., 2010b). Autonomous $f$$CO_2$ and pH sensors are commercially available and in use (Lefèvre et al., 1993; Seidel et al., 2008), and most of them use spectrophotometric measurements of pH in artificial test solutions of known alkalinity (Byrne et al., 2010b). A number of new chemical sensors have been introduced for the carbonate system. Portable underwater membrane inlet mass spectrometry (MIMS) could offer the simultaneous determination of the $f$$CO_2$ and DIC (Byrne et al., 2010b). These systems are available at various platforms (Wenner et al., 2004; Camilli and Hemond, 2004; Schlueter and Gentz, 2008). The use of MIMS also provides levels of gases such as oxygen and nitrogen and has the possibility of
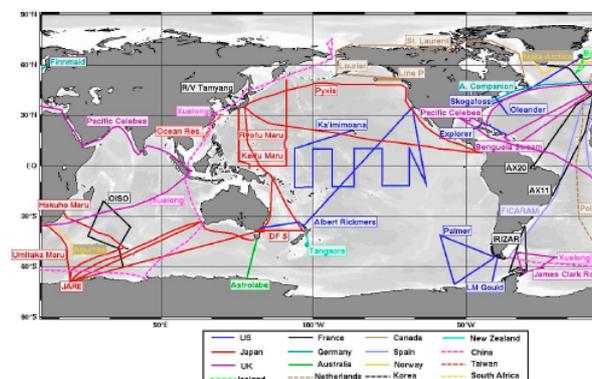


**Figure 5**. *Underway Volunteer Observing Ship Network.*

measuring the carbon isotope composition of DIC (Byrne et al., 2010b). In addition to the network of ocean observatories, the present ocean acidification monitoring network could profit from measurements on ships (Figure 5) equipped with carbon system sensors and ancillary technologies (e.g. autonomous water samplers, nutrient analyzers).

In monitoring the health of ecosystems a number of physiological indicators can be measured from instrumental moorings in ecosystem observing systems (Brainard et al., 2010). For example, in coral reef systems, pulse amplitude modulating (PAM) fluorometry is the most extensively used approach to measure photosystem II activity. In addition to the network of instruments measuring physico-chemical conditions, satellite and ship-based bathymetry, calcification rates, habitat mapping and visual observations of plants and animals contribute to the integrated coral reef ecosystem and mapping observations in the US Caribbean (Kendall et al., 2004; Monaco et al, 2007, Brainard et al., 2008). Examples of some developing observation systems are the Coral Reef Ecosystem Observing System, the Moorea Coral Reef Long Term Ecological Research, the Great Barrier Reef Ocean Observing System, the Coral Reef Environmental Observatory Network, and the Global Coral Reef Monitoring Network (Brainard et al., 2010).

The coastal ocean is more susceptible to anthropogenic forcing than the open ocean. In coastal regions, the effect of upwelling and riverine input can shift carbon cycle dynamics very rapidly, particularly in response to changes in nutrients and organic carbon inputs (McKenzie et al., 2004), which can lead to long term changes in $CO_2$ sequestration (Gypens et al 2009; Borges et al., 2010). The dynamics in the coastal environment has so far only been investigated through a few observations (Omar et al., 2003; Thomas et al., 2007) and models (Mackenzie et al., 2004; Gypens et al., 2009; Hauri et al., 2009). Similar dynamics have been observed in island coastal ecosystems not associated with continental shelf settings (Bates, 2002; Fagan and McKenzie, 2007; Salisbury et al., 2008; Feely et al. 2010b) and although many of these environments are generally not part of global carbon cycle synthesis studies, they can be susceptible to anthropogenic impacts (Borges et al., 2010).

New moored buoys equipped with carbon system sensors and ancillary technologies (e.g. autonomous water samplers, nutrient analyzers, oxygen, Fast Repetition Rate Fluorometry FRRF for phytoplankton photophysiology) for the assessment of effects of ocean acidification should be added to the present carbon network. These open-ocean monitoring systems, when thus equipped, will provide verification for open ocean large-scale biogeochemical models. Coastal data will verify nested high resolution coastal models. Carbon
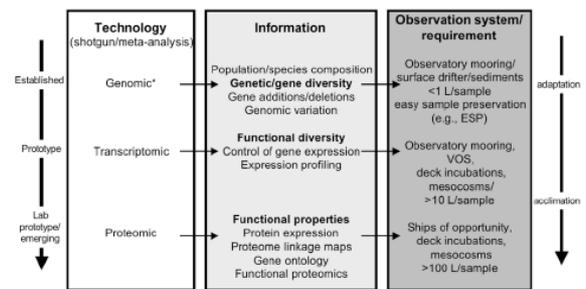


*Figure 6*. *The application of '-omics' tools to ecological and biogeochemical questions as part of the ocean observation network monitoring program.*

system sensors could also be deployed on floats and gliders to resolve shorter space-time scale variability of the upper ocean. Sites which also deploy deep sediment traps offer additional advantages, in allowing the links between calcification and biological carbon sequestration to the deep to be evaluated (Oschlies et al., 2008), and by providing seasonally resolved sampling of biogenic carbonate forming organisms, such as foraminifera which have been shown to exhibit reduced shell thicknesses in response to acidification (Moy et al., 2009).

### 7.4. The emerging '-omics' technologies

The application of molecular tools traditionally used in the biomedical field is revolutionizing the field of oceanography. Genomics, transcriptomics, and proteomics are rapidly transforming marine biology and biogeochemical studies (Figure 6). Shotgun methods have enabled assessment of the diversity of populations, the most striking example being Venter's metagenomics approach to dissecting the population structure of microbial populations in the Sargasso Sea (Venter et al., 2004; Delong et al., 2006, Sogin et al., 2006 and references therein). Research has transitioned from 'static' descriptive studies of single genes, proteins or metabolites to a more ecological approach, involving the simultaneous study of many levels of organization (from molecules represented in the mixed cell suspension (shotgun approach) through to whole organisms, populations and communities) (Hollywood et al., 2006, Joyce & Palsson 2006). However, in order to achieve the full potential, an integration of these molecular data with traditional ecological and biogeochemical approaches is required (Doney et al., 2004). The information that can be acquired with these approaches includes estimates of the genomic diversity within populations, up- and down-regulation of biological processes under different environmental conditions, and potentially direct rates of evolution to environmental selection pressure. If tested in the field, using the three levels of molecular regulation (DNA, RNA, proteins) would implicitly identify tipping points of tolerance. Combining tightly-controlled laboratory experiments with field-testing of laboratory results

would provide information at the strain, population, and community levels. While genomic protocols have been optimized for field studies (Venter et al., 2004), field proteomics is still in its infancy. Another limitation is the access to the appropriate bioinformatics resources and the training required for data interpretation. In the immediate future, marine scientists dealing with biological systems will need these skills and thus appropriate training.

## 8. CHALLENGES

One of the biggest challenges facing the community is to unveil the mechanisms behind biological adaptation over realistic time frames and thereby determine which species do or do not have the ability to adapt to future ocean acidification. Most experimental approaches used to date only address physiological responses to environmental selection pressure rather than long-term adaptation. There is an urgent need to conduct manipulations involving time-scales of multiple generations (cell division, generation of organisms) and environmental change at rates representative of those experienced by biota in the open ocean (Boyd et al., 2008). Monitoring potential adaptation in real time in the field, particularly in those areas of high susceptibility to ocean acidification (polar latitudes, upwelling zones) will provide information central to representing and forecasting the repercussions of ocean acidification on biota. Information from these platforms will be used to calibrate the findings in the laboratory experiments/mesocosms with strains/populations and to inform policy makers and marine resource managers. Data repositories of detailed carbonate chemistry, biological performance and molecular adaptation to environmental selection pressure will not only provide first hand information about natural selection processes in real time but will also answer fundamental questions of how changes in carbon chemistry alter the abundance and physiology of functional groups. While work with single strains/species provides valuable information about regulation of processes, it does not account for the complexity of natural populations, physical transport effect, interactions between bacteria and viruses and eukaryotic phytoplankton, mortality, etc.

Many countries are presently engaged in ocean acidification research and monitoring activities, for example, the EU projects EPOCA, MEECE and MedSeA, the German BIOACID project, the UK Ocean Acidification Research Programme, US (emerging program supported by NSF, NOAA, NASA, USGS) , and Japan MoE and MEXT Ocean Acidification Research Programmes. The proposed activities will require a coordinated international research effort that is closely linked with other international carbon research programs, such as the CLIVAR/$CO_2$ Repeat Hydrography Program. The

SOLAS-IMBER Working Group on Ocean Acidification (http://www.imber.info/C_WG_SubGroup3.html) and the IOCCP could play roles to coordinate and integrate, at the international level, the research, training and outreach activities. The Global Ocean Acidification Observation Network will benefit from and interface with the data synthesis activities, data archiving and international data management activities of the carbon and ocean acidification programs. The main role of the Global Ocean Acidification Observation Network is to gain a robust understanding of the chemical and biological impacts of ocean acidification by conducting (1) time-series measurements in open ocean and coastal observatories at several levels of organization from molecular to ecosystem level; (2) *in-situ* manipulations and mesocosm experiments, and autonomous measurements aboard voluntary observing ships; and (3) global and regional monitoring using satellite data. Cooperation with well established international programs such as the IODP, and forming a global network with good spatial and temporal coverage will be central to its success. The application of genomic, transcriptomic and proteomic approaches to studying oceanic ecosystem may open new opportunities for understanding the organisms control on elemental cycles though time. Robotic *in-situ* devices deployed on moorings can be powerful tools and are now available as autonomous samplers, to report on genomic data of microbial community composition (Greenfield et al., 2006; 2008; Scholin et al, 2008). Building this global time series to assess changes in ocean chemistry and biology will improve coupling between biogeochemistry, physiology, and modelling and play a major role in providing sound scientific evidence to society and decision makers on the consequences of future acidification of oceans, seas and coastal waters and on the time scales required for $CO_2$ emissions reduction to reduce the risks from acidification.

## 9. CONCLUDING REMARKS

The rate of change in ocean pH and carbon chemistry is expected to accelerate over this century unless societal decisions reduce $CO_2$ emissions dramatically. Quantifying how these changes are going to affect ecosystem functioning, ocean biogeochemistry and human society is a priority. Emerging technology in the oceanographic community is revolutionizing the way we sample the oceans. An integrated international interdisciplinary program of ship-based hydrography, time-series moorings, floats and gliders with carbon system, pH and oxygen sensors, and ecological surveys is already underway. This network will incorporate new technology to investigate changes at many levels of organization (from molecular to ecosystem level to global) to determine the extent of the large-scale

changes in the carbon chemistry of seawater and the associated biological responses to ocean acidification in open ocean as well as coastal environments. Many countries have endorsed these activities, and it will be the responsibility of leading countries and institutions to ensure continuity of these efforts in ocean acidification research and monitoring activities. The Global Ocean Acidification Observation Network will benefit from and interface with the data synthesis activities, data archiving and international data management activities of the carbon and ocean acidification programs.

## Acknowledgements

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