

TOWARDS AN INTEGRATED GLOBAL OCEAN ACIDIFICATION OBSERVATION NETWORK

M. Debora Iglesias-Rodriguez⁽¹⁾, Kenneth R.N. Anthony⁽²⁾, Jella Bijma⁽³⁾, Andrew G. Dickson⁽⁴⁾, Scott C. Doney⁽⁵⁾, Victoria J. Fabry⁽⁶⁾, Richard A. Feely⁽⁷⁾, Jean-Pierre Gattuso⁽⁸⁾, Kitack Lee⁽⁹⁾, Ulf Riebesell⁽¹⁰⁾, Toshiro Saino⁽¹¹⁾ and Carol Turley⁽¹²⁾

⁽¹⁾ School of Ocean and Earth Science, National Oceanography Centre, European Way, Southampton, SO14 3ZH, UK, Email: dir@noc.soton.ac.uk

⁽²⁾ Global Change Institute, The University of Queensland, St Lucia QLD 4072 Australia, Email: k.anthony@uq.edu.au

⁽³⁾ Alfred Wegener Institute, Am Handelshafen 12, D-27570 Bremerhaven, (Building E-2055), Germany, Email: Jelle.Bijma@awi.de

⁽⁴⁾ Scripps Institution of Oceanography, University of California, San Diego, 9500 Gilman Drive, La Jolla, CA 92093-0244, USA, Email: adickson@ucsd.edu

⁽⁵⁾ Woods Hole Oceanographic Institution, 266 Woods Hole Rd., MS# 25, Woods Hole, Ma. 02543, USA, Email: sdoney@whoi.edu

⁽⁶⁾ Department of Biological Sciences, California State University San Marcos, 333 South Twin Oaks Valley Road, San Marcos, CA 92096-0001, USA, Email: fabry@csusm.edu

⁽⁷⁾ Pacific Marine Environmental Laboratory, National Oceanic and Atmospheric Administration, 7600 Sand Point Way NE, Seattle, WA 98115, USA, Email: richard.a.feely@noaa.gov

⁽⁸⁾ Observatoire Océanologique, Laboratoire d'Océanographie, CNRS-UPMC, B. P. 28, F-06234 Villefranche-sur-Mer Cedex, France, Email: gattuso@obs-vlfr.fr

⁽⁹⁾ Pohang University of Science and Technology, School of Environmental Science and Engineering, Pohang, 790-784, Republic of Korea, Email: ktl@postech.ac.kr

⁽¹⁰⁾ Leibniz Institute of Marine Sciences (IFM-GEOMAR), Marine Biogeochemistry-Biological Oceanography-Düsternbrooker Weg 20, 24105 Kiel, Germany, Email: uribesell@ifm-geomar.de

⁽¹¹⁾ Environmental Biogeochemical Cycle Research Program (EBCRP), Research Institute for Global Change (RIGC), Japan Agency for Marine-Earth Science and Technology (JAMSTEC), Japan, Email: tsaino@jamstec.go.jp

⁽¹²⁾ Plymouth Marine Laboratory, Registered Office: Prospect Place, The Hoe, Plymouth PL1 3DH, U.K., Email: CT@pml.ac.uk

ABSTRACT

The increase in atmospheric carbon dioxide (CO₂), 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 CO₂ emissions are restricted dramatically. The rate of CO₂ 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 CO₂. 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/CO₂ 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 (CO₂)

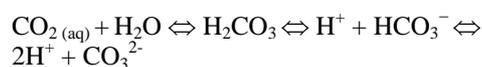
from approximately 280 parts per million (ppm) at the end of the 19th century to the current levels of 390 ppm CO₂ (2010 levels). During this time, the oceans have absorbed about one-third of the anthropogenic carbon emissions (Sabine et al. 2004), which represents a great advantage to the Earth's biosphere because the ocean uptake of CO₂ reduces greenhouse gas levels in the atmosphere, potentially ameliorating global warming. When CO₂ dissolves in seawater, the concentrations of carbon dioxide ([CO₂]) and bicarbonate ([HCO₃⁻]) increase and both the pH and the concentration of carbonate ions ([CO₃²⁻]) decrease. This process, referred to as ocean acidification (Fig. 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 CO₂ on the CO₂ levels in the surface ocean pCO₂ as is shown by the surface ocean pCO₂ following the trend in atmospheric CO₂ increase over the past 20 years (Fig. 1). While the current levels of CO₂ are not unprecedented in the history of Earth, current CO₂ 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 CO₂ 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 CO₂ (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 CO₃²⁻ in seawater, which is essential for the production of calcium carbonate (CaCO₃) 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 (Ω) of the two CaCO₃ polymorphs, calcite and aragonite, [Ω = [Ca²⁺] [CO₃²⁻] / K'_{sp} (where K'_{sp} is the apparent solubility product constant for calcite or aragonite) decreases. It has been suggested that the values for Ω 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 Ω and pH, if atmospheric CO₂ 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 CO₂ 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 CO₂ emission mitigation.

2. SOME FACTS ABOUT OCEAN ACIDIFICATION

Results from the global ocean CO₂ surveys over the past two decades demonstrate that ocean acidification is an indisputable consequence of rising atmospheric CO₂. Seawater carbonate chemistry is controlled by a series of chemical equilibria, invasion and evasion of CO₂ across the air-sea interface, exchange, dissolution and precipitation reactions of CaCO₃. Atmospheric CO₂ equilibrates with dissolved CO₂ in seawater [CO₂ (atmos) ⇌ CO₂ (aq)], and any increase in the partial pressure of CO₂ in the atmosphere reaches equilibration with the ocean surface water within about a year. CO₂ reacts with seawater to form carbonic acid (H₂CO₃), a weak acid. A major fraction of the H₂CO₃ dissociates into hydrogen ions (H⁺) and bicarbonate ions (HCO₃⁻). Some of the H⁺ reacts with carbonate ions (CO₃²⁻) to produce HCO₃⁻ ions. As a result, CO₂ uptake by the oceans causes an increase in H⁺, and consequently lowers pH and CO₃²⁻ concentrations:



While the CO₂ hydration reaction is relatively slow, the reactions between H⁺ and HCO₃⁻ and CO₃²⁻ are extremely fast. The formation of H₂CO₃ occurs within 10s of seconds and the interconversion of HCO₃⁻ and CO₃²⁻ takes place within microseconds. For surface open ocean conditions, about 90% of the total carbon is in the form of the bicarbonate anion (HCO₃⁻), ~9% as carbonate (CO₃²⁻), and ~1% remains as CO_{2(aq)} and H₂CO₃.

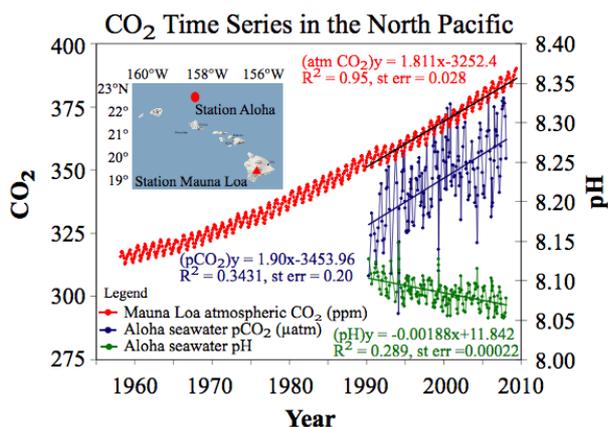


Figure 1. Time series of atmospheric CO₂ at Mauna Loa (in parts per million, ppm) and surface ocean pH and pCO₂ (μatm) at Ocean Station Aloha in the subtropical North Pacific Ocean. Note that the increase in oceanic CO₂ over the last 17 years is consistent with the atmospheric increase within the statistical limits of the measurements. Mauna Loa data: Dr. Pieter Tans, NOAA/ESRL (National Oceanic and Atmospheric Administration/Earth System Research Laboratory)

(<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: $\text{Ca}^{2+} + \text{CO}_3^{2-} \rightleftharpoons \text{CaCO}_3(\text{s})$. The saturation state (Ω) affects the extent of biologically-mediated calcification although the exact relationship between carbonate precipitation and Ω remains unclear. The term Ω 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., 2009). Many of the marine organisms producing skeletons or body parts of solid-phase CaCO₃ are known to be sensitive to the concentration of CO₃²⁻ 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 Ω 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 CO₂ fluxes between the upper ocean and the atmosphere: photosynthesis utilizes CO₂ at the surface and thus increases the seawater pH while respiration releases CO₂ in the surface ocean and throughout the water column: $\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{CH}_2\text{O} + \text{O}_2$. Calcification

uses CO₃²⁻ and HCO₃⁻ but since HCO₃⁻ concentration in seawater is more than an order of magnitude greater than that of CO₃²⁻ in seawater, it is thought that most calcifiers are able to utilize HCO₃⁻. Bicarbonate utilization in the calcification process produces CO₂ as a byproduct: $2\text{HCO}_3^- + \text{Ca}^{2+} \rightleftharpoons \text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O}$ [only about 0.6 moles of CO₂ are released for each mole of CaCO₃ 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 CO₂, thereby sequestering CO₂ 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 et al, 2010). Additionally, ocean acidification-driven changes in phytoplankton physiology may have an effect on nutrient (e.g., N, P and C) utilization and oxygen consumption. Although the focus of global carbon monitoring programs is on measuring CO₂, oxygen measurements are required particularly when investigating the effect of ocean acidification on biologically-relevant processes involving the cycling of CO₂ and O₂. 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 CO₂ or O₂. Therefore, monitoring not only CO₂ but also O₂ 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 pCO₂ and

atmospheric CO₂ agree well (Fig. 1), and further indicate that the uptake of anthropogenic CO₂ is the major cause for long-term increases in dissolved inorganic carbon (DIC) and decreases in CaCO₃ 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 (Fig. 2). Here the seasonal upwelling along the coast brings CO₂-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 CO₂ resulting from natural respiration processes in the subsurface layers, is also enriched with anthropogenic CO₂ from gas exchange and vertical mixing. The CO₂ 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.

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

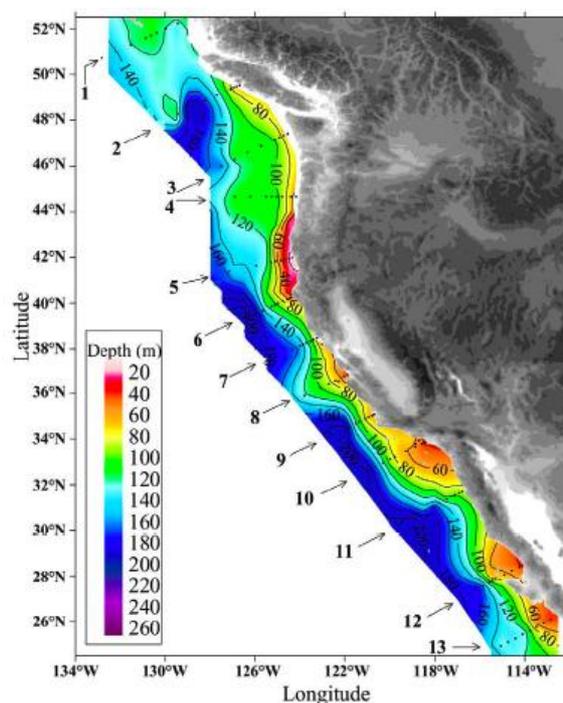


Figure 2. Distribution of the depths of the undersaturated water (aragonite saturation < 1.0; pH < 7.75) on the continental shelf of western North America from Queen Charlotte Sound, Canada to San Gregorio Baja California Sur, Mexico. On transect lines 5 the corrosive water reaches all the way to the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

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 CO₂ levels increase in seawater, those species that have evolved mechanisms to acquire inorganic carbon under low CO₂ (CO₂-concentrating mechanisms) may be outnumbered by those relying largely on CO₂. In seagrasses, growth and light-saturated photosynthetic rates are also increased under high CO₂ 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

Physiological Response	Major group	# species studied	Response to increasing CO ₂				References
			a	b	c	d	
Calcification	Coccolithophores	5	9	3	3	3	11, 34, 35, 44, 95, 61, 118, 128, 162/ 97, 83, 140, 157, 118, 126/9, 104, 105
	Planktonic Foraminifera	2	3	-	-	-	12, 13, 145/-/-/-
	Molluscs	6	5	-	-	-	64, 67, 76, 110, 121/-/-/-
	Echinoderms	3	3	3	-	1	27, 43, 114, 166, 157/-/131
	Corals	12	11	-	1	-	7, 32, 63, 72, 73, 84, 89, 94, 101, 102, 107/-/132/-
	Coralline red algae	1	1	-	-	1	98/-/131
Arthropods	2	2	1	-	-	3, 100/131/-/-	
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 CO₂ for each of the groups (from Doney et al., 2009). * indicates natural assemblages.

temperature and CO₂ appeared to control phytoplankton population composition (Tortell et al., 2008). Also, some coral species in mesocosm experiments show enhanced productivity under CO₂ up to 560 ppm, but severely reduced productivity under CO₂ 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 CO₂ in *Trichodesmium* sp. (Barcelos e Ramos et al., 2007; Hutchins et al., 2007) (Fig. 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 CO₃²⁻ from HCO₃⁻ 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 CO₂ 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 Ca²⁺ in seawater (~10.2 mmol kg⁻¹), carbonate ions are likely the limiting substrate in marine calcification (Langdon and Atkinson, 2005). And since the average concentration of CO₃²⁻ in open ocean surface seawater (~0.19 mmol kg⁻¹) is approximately one order of magnitude smaller than concentration of HCO₃⁻ in seawater (~1.9 mmol kg⁻¹), it is perhaps expected that the ability to utilize HCO₃⁻ 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 pCO₂ 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 makeup 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 CO₂ ON DECADAL TIME SCALES

Measurements of the CO₂ 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 et al., 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*CO₂, 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., *p*CO₂ 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 (Ocean Observatories Initiative), IOCCP (International Ocean Carbon Coordination Project), and the SOLAS/IMBER (Surface Ocean - Lower Atmosphere Study/Integrated Marine Biogeochemistry and Ecosystem Research) 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 CO₂-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 CO₂ survey conducted by WOCE-JGOFS (World Ocean Circulation Experiment-Joint Global Ocean Flux Study) programs in the 1990s which resulted in novel high quality data sets with global coverage (Wallace, 2001; Sabine et al., 2004). Since then, GLODAP (Global Ocean Data Analyses Project) has provided unified global synthesis data on naturally occurring and anthropogenically induced CO₂ (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) (O₂ 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 O₂:CO₂ 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 is required (e.g., Gruber et al., 2010). Oxygen is a candidate for inclusion in the measured parameters of the Argo (Global array of free-drifting profiling floats) float program (Claustre et al., 2010, Gruber et al., 2010) Additionally, working together with the IODP

community will provide the temporal dimension that is currently limiting our assessment of long term trends in CO₂, O₂ 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 (Woods Hole Oceanographic Institution) long-corer can be used in assessing changes during glacial/interglacial transitions in platforms such as IODP (Integrated Ocean Drilling Program). 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 (Integrated Ocean Observing System), GOOS (Global Ocean Observing System), OceanSITES (OCEAN Sustained Interdisciplinary Time series Environment Observation System) 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 pCO₂, 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 CaCO₃ saturation states and rates of CaCO₃ production and dissolution. Sensors for DIC and TA are desirable for detecting changes in the marine inorganic carbon system and deposition of other non-CO₂ 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 CO₂ and reduced transport of oxygen from the ocean

surface to its interior (Gruber et al., 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

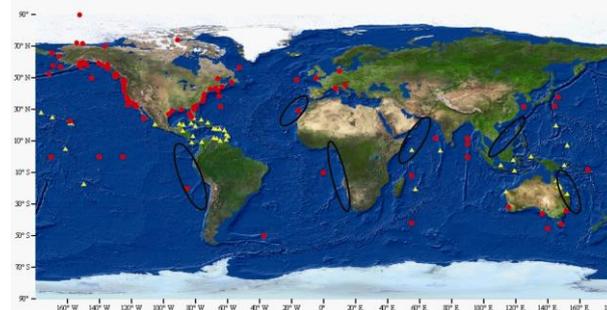


Figure 4. Potential ocean acidification monitoring sites in open-ocean and coastal regions, and potential coral reef ocean acidification monitoring sites. The station locations are given in Feely et al., 2010. Red circles represent deployed or planned open-ocean monitoring sites; yellow triangles represent 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 (Fig. 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:
 - 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);
 - production rates including calcification, silicification, nitrogen fixation, photosynthesis using direct measurements in combination with satellite-derived calculations;
 - 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 CO₂ manipulations in mesocosm, shipboard 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 CO₂ 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 CO₂ (*f*CO₂) combined with sensors for total alkalinity or DIC are the best approach to characterize the carbonate system (Byrne et al., 2010b). Autonomous *f*CO₂ 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*CO₂ 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 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 (Fig. 5) equipped with carbon system sensors

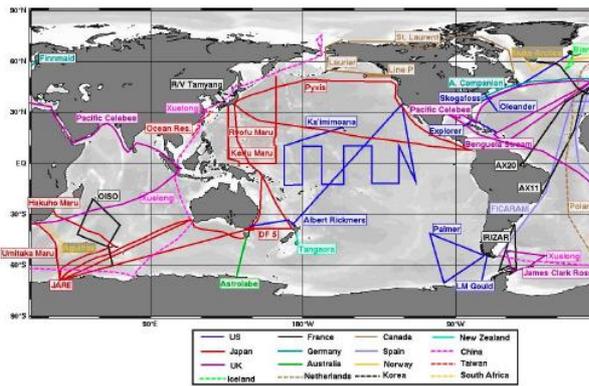


Figure 5. Underway Volunteer Observing Ship Network.

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 CO₂ 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

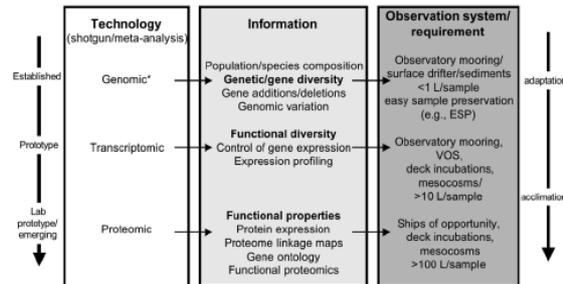


Figure 6. The application of '-omics' tools to ecological and biogeochemical questions as part of the ocean observation network monitoring program.

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 (Fig. 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 and 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 (European Project on Ocean Acidification), MEECE (Marine Ecosystem Evolution in a Changing Environment) and MedSeA (MEDiterranean Sea Acidification), the German BIOACID (Biological Impacts of Ocean ACIDification) project, the UK Ocean Acidification Research Programme, US (emerging program supported by NSF (National Science Foundation.), NOAA (National Oceanic and Atmospheric Administration), NASA (National Aeronautics and Space Administration), USGS (United States Geological Survey)), and Japan MoE (Japan Ministry of Environment) and MEXT (Ministry of Education, Culture, Sports, Science and Technology) 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/CO₂ (Climate Variability and Predictability/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 CO₂ 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 CO₂ 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

This work is a contribution to the European Project on Ocean Acidification (EPOCA) funded by the European Community's Seventh Framework Programme (FP7/2007-2013 grant n° 211384), to the UK Ocean Acidification Research Programme (UKOARP) and funded by Natural Environment Research Council, the Department of Environment, Food and Rural Affairs and the Department of Energy and Climate Change. The U.S. co-authors gratefully acknowledge support from NSF, NOAA and NASA.

REFERENCES

1. Alvarado-Alvarez, R., M. C. Gould and J. L. Stephano (1996). Spawning, in vitro maturation, and changes in oocyte electrophysiology induced by serotonin in

- Tivela stultorum, Development and reproduction 190, 322-328.
2. Anthony, K. R. N., D.I. Kline, G. Diaz-Pulido, S. Dove, and O. Hoegh-Guldberg (2008). Ocean acidification causes bleaching and productivity loss in coral reef builders, PNAS 105 17442-17446.
3. Arnold, K. E., H. S. Findlay, J. I. Spicer, C. L. Daniels, and D. Boothroyd (2009). Effect of CO₂-related acidification on aspects of the larval development of the European lobster, *Homarus gammarus* (L.). Biogeosci. 6:1747-1754.
4. Barcelos e Ramos, J., H. Biswas, K. G. Schulz, J. LaRoche and U. Riebesell (2007). Effect of rising atmospheric carbon dioxide on the marine nitrogen fixer *Trichodesmium*, Global Biogeochemical Cycles, 21, GB2028, 6 PP., doi:10.1029/2006GB002898.
5. Barcelos e Ramos, J., M. N. Müller and U. Riebesell (2010). Short-term response of the coccolithophore *Emiliana huxleyi* to an abrupt change in seawater carbon dioxide concentrations, Biogeosciences 7, 177-186.
6. Barry, J., B.A. Seibel, J. Drazen, M. Tamburri, C. Lovera and P. Brewer (2002). Field experiments on direct ocean CO₂ sequestration: the response of deep-sea faunal assemblages to CO₂ injection at 3200 m off Central California, EOS Transactions, AGU 83, OS51F-02.
7. Bates, N. R. (2002). Seasonal variability of the impact of coral reefs on ocean CO₂ and air-sea CO₂ exchange, Limnol. Oceanogr., 47, 43-52.
8. Bates, N. R. (2007). Interannual variability of the oceanic CO₂ sink in the subtropical gyre of the North Atlantic Ocean over the last 2 decades, J. Geophys. Res., 112, C09013, doi:10.1029/2006JC003759.
9. Bates, N. R. and A. J. Peters (2007). The contribution of atmospheric acid deposition to ocean acidification in the subtropical North Atlantic Ocean, Marine Chemistry 107, 547-558, doi:10.1016/j.marchem.2007.08.002.
10. Bates, N. R., J. T. Mathis and L. Cooper (2009). The effect of ocean acidification on biologically induced seasonality of carbonate mineral saturation states in the Western Arctic Ocean, J. Geophys. Res.-Oceans, 114, C11007, doi:10.1029/2008JC004862.
11. Bierman, A. and A. Engel (2010). Effect of CO₂ on the properties and sinking velocity of aggregates of the coccolithophore *Emiliana huxleyi*, Biogeosciences 7, 1017-1029.
12. Bijma, J., H. J. Spero and D. W. Lea (1999). Reassessing foraminiferal stable isotope geochemistry: impact of the oceanic carbonate system (experimental results), from Fischer, G. and Wefer, G. (eds), Use of proxies in Paleoceanography: examples from the South Atlantic, Springer-Verlag, Berlin Heidelberg, 489-512.

13. Bijma, J., B. Hönisch and R. E. Zeebe (2002). Impact of the ocean carbonate chemistry on living foraminiferal shell weight: comment on "Carbonate ion concentration in glacial-age deep waters of the Caribbean Sea" by W. S. Broecker and E. Clark, *Geochem. Geophys. Geosy.* 3, 1064, doi:10.1029/2002GC000388.
14. Blackford, J.C. (2010). Predicting the impacts of ocean acidification: Challenges from an ecosystem perspective, *Journal of Marine Systems*, doi:10.1016/j.jmarsys.2009.12.016.
15. Borges, A. & Co-Authors (2010). "A Global Sea Surface Carbon Observing System: Inorganic and Organic Carbon Dynamics in Coastal Oceans" in these proceedings (Vol. 2), doi:10.5270/OceanObs09.cwp.07.
16. Boyd P., S. C. Doney, R. Strzepke, J. Dusenberry, K. Lindsay, I. Fung (2008). Climate-mediated changes to mixed layer properties in the Southern Ocean: assessing the phytoplankton response. *Biogeosciences* 5:847–64.
17. Brainard, R.E., J. Asher, J. Gove, J. Helyer, et al., Eds. (2008). *Coral Reef Ecosystem Monitoring Report for American Samoa: 2002–2006*, NOAA NMFS Pacific Islands Fisheries Science Center Coral Reef Ecosystem Division, Honolulu, HI, 510 pp. 31.
18. Brainard, R. & Co-Authors (2010). "An International Network of Coral Reef Ecosystem Observing Systems (I-CREOS)" in these proceedings (Vol. 2), doi:10.5270/OceanObs09.cwp.09.
19. Brierley, A.S. and M. J. Kingsford (2009). Impacts of Climate Change on Marine Organisms and Ecosystems, *Current Biology* 19, R602-R614, doi:10.1016/j.cub.2009.05.046.
20. Byrne, R. H., S. Mecking, R. A. Feely and X. Liu (2010a). Direct observations of basin-wide acidification of the North Pacific Ocean, Direct observations of basin-wide acidification of the North Pacific Ocean, *Geophysical Research Letters* 37, L02601, 5, doi:10.1029/2009GL040999.
21. Byrne, R. & Co-Authors (2010b). "Sensors and Systems for In Situ Observations of Marine Carbon Dioxide System Variables" in these proceedings (Vol. 2), doi:10.5270/OceanObs09.cwp.13.
22. Caldeira K. and M. E. Wickett (2003). Anthropogenic carbon and ocean pH. *Nature* 425:365.
23. Caldeira, K. and M. E. Wickett (2005). Ocean model predictions of chemistry changes from carbon dioxide emissions to the atmosphere and ocean. *J. Geophys. Res.* 110, C09S04, doi:10.1029/2004JC002671.
24. Camilli, R. and H. F. Hemond (2004). NEREUS/Kemonaut, a Mobile Autonomous Underwater Mass Spectrometer, *Trends Anal. Chem.* 23, 307–313.
25. Cao, L. and K. Caldeira, Atmospheric CO₂ stabilization and ocean acidification, *Atmospheric CO₂ stabilization and ocean acidification* *Geophysical Research Letters* 35, L19609, 5 PP., 2008, doi:10.1029/2008GL035072
26. Chung S. N., K. Lee, R. A. Feely, C. L. Sabine, F. J. Millero, R. Wanninkhof, J. L. Bullister, R. M. Key, and T.-H. Peng (2003). Calcium carbonate budget in the Atlantic Ocean based on water column inorganic carbon chemistry. *Glob. Biogeochem. Cycles* 17:1093.
27. Clark, D., M. Lamare and M. Barker (2009). Response of sea urchin pluteus larvae (Echinodermata: Echinoidea) to reduced seawater pH: a comparison among a tropical, temperate, and a polar species, *Marine Biology* 156, 1125–1137.
28. Claustre, H. & Co-Authors (2010). "Bio-Optical Profiling Floats as New Observational Tools for Biogeochemical and Ecosystem Studies: Potential Synergies with Ocean Color Remote Sensing." in these proceedings (Vol. 2), doi:10.5270/OceanObs09.cwp.17.
29. Comeau, S., G. Gorsky, R. Jeffree, J.-L. Teyssi and J.-P. Gattuso, 2009, Impact of ocean acidification on a key Arctic pelagic mollusc (*Limacina helicina*), *Biogeosciences*, 6, 1877–1882.
30. Cooley, S. R. and S. C. Doney, 2009, Anticipating ocean acidification's economic consequences for commercial fisheries. *Environmental Research Letters* 4, 024007, doi:10.1088/1748-9326/4/2/024007.
31. Cooley, S. R., H. L. Kite-Powell and S. C. Doney (2009). Ocean acidification's potential to alter global marine ecosystem services. *Oceanography* 22:172–181.
32. Cooper, T. F., G. De'ath, K. E. Fabricius and J. M. Lough (2008). Declining coral calcification in massive Porites in two nearshore regions of the northern Great Barrier Reef, *Global Change Biology* 14, 529–538.
33. Czerny, J., J. Barcelos e Ramos and U. Riebesell (2009). Seawater carbonate chemistry and processes during experiments with cyanobacterium *Nodularia spumigena*, *Biogeosciences* 6, 1865–1875.
34. De Bodt, C., N. Van Oostende, J. Harlay, K. Sabbe and L. Chou (2010). Individual and interacting effects of pCO₂ and temperature on *Emiliana huxleyi* calcification: study of the calcite production, the coccolith morphology and the coccosphere size, *Biogeosciences* 7, 1401–1412.
35. Delille, B., J. Harlay, I. Zondervan, S. Jacquet, L. Chou, R. Wollast, R. G. J. Bellerby, M. Frankignoulle, A. Vieira Borges, U. Riebesell and J.-P. Gattuso (2005). Response of primary production and calcification to changes of pCO₂ during experimental blooms of the coccolithophorid *Emiliana huxleyi*, *Glob. Biogeochem. Cycles* 19, GB2023, doi:10.1029/2004GB002318.
36. DeLong, E. F., C. M. Preston, T. Mincer, V. Rich, S. J. Hallam, N.-U. Frigaard, A. Martinez, M. B. Sullivan,

- R. Edwards, B. Rodriguez Brito, S. W. Chisholm and D. M. Karl (2006). Community genomics among stratified microbial assemblages in the ocean's interior, *Science* 311:496–503.
37. Desrosiers, R. R., J. Desilets and F. Dube (1996). Early developmental events following fertilization in the giant scallop *Placopecten magellanicus*, *Can. J. Fish. Aquat. Sci.* 53, 1382-1392.
 38. Doney, S. C., M. R. Abbott, J. J. Cullen, D. M. Karl and L. Rothstein (2004). From genes to ecosystems: the ocean's new frontier. *Front. Ecol. Environ.* 2, 457–466.
 39. Doney, S. C., N. Mahowald, I. Lima, R.A. Feely, F.T. Mackenzie, J.-F. Lamarque, and P.J., Rasch (2007). The impact of anthropogenic atmospheric nitrogen and sulfur deposition on ocean acidification and the inorganic carbon system, *Prod. Nat. Acad. Sci. USA*, 104, 14580-14585, doi:10.1073/pnas.0702218104.
 40. Doney, S.C., V. J. Fabry, R. A. Feely and J. A. Kleypas (2009). Ocean acidification: the other CO₂ problem, 2009, *Annual Review of Marine Science* 1: 169-192, doi:10.1146/annurev.marine.010908.163834.
 41. Doney, S.C. (2010). The growing human footprint on coastal and open-ocean biogeochemistry, *Science* 328: 1512-1516.
 42. Dore, J. E., R. Lukas, D.W. Sadler, M.J. Church, and D.M. Karl (2009). Physical and biogeochemical modulation of ocean acidification in the central North Pacific. *Proceedings of the National Academy of Sciences of the United States of America* 106:12235–12240.
 43. Dupont, S., J. Havenhand, W. Thorndyke, L. Peck and M. Thorndyke (2008). Near-future level of CO₂-driven ocean acidification radically affects larval survival and development in the brittlestar *Ophiothrix fragilis*. *Mar Ecol Prog Ser* 373: 285–294.
 44. Engel, A., I. Zondervan, K. Aerts, L. Beaufort, A. Benthien et al. (2005). Testing the direct effect of CO₂ concentration on a bloom of the coccolithophorid *Emiliana huxleyi* in mesocosm experiments, *Limnol. Oceanogr.* 50, 493-507.
 45. Fabry, V. J., B. A. Seibel, R. A. Feely and J. C. Orr (2008). Impacts of ocean acidification on marine fauna and ecosystem processes. *ICES. J. Mar. Sci.* 65:414–32.
 46. Fagan, K. E. and F. T. Mackenzie (2007). Air–sea CO₂ exchange in a subtropical estuarine coral reef system, Kaneohe Bay, Oahu, Hawaii, *Marine Chemistry* 106, 174–191.
 47. Feely R. A. and C. T. A. Chen (1982). The effect of excess CO₂ on the calculated calcite and aragonite saturation horizons in the northeast Pacific. *Geophys. Res. Lett.* 9:1294–97.
 48. Feely, R.A., R.H. Byrne, P.R. Betzer, J.F. Gendron, and J.G. Acker (1984). Factors influencing the degree of saturation of the surface and intermediate waters of the North Atlantic Ocean with respect to aragonite, *J. Geophys. Res.* 89(C6): 10631-10640.
 49. Feely R. A., R. H. Byrne, J. G. Acker, P. R. Betzer, C. T. A. Chen, et al. (1988). Winter summer variations of calcite and aragonite saturation in the northeast Pacific. *Mar. Chem.* 25:227–41.
 50. Feely R. A., C. L. Sabine, K. Lee, F. J. Millero, M. F. Lamb, et al. (2002). In situ calcium carbonate dissolution in the Pacific Ocean. *Glob. Biogeochem. Cycles* 16:1144.
 51. Feely R. A., C. L. Sabine, K. Lee, W. Berelson, J. Kleypas, et al. (2004). Impact of anthropogenic CO₂ on the CaCO₃ system in the oceans. *Science* 305:362–66.
 52. Feely R. A., C. L. Sabine, J. M. Hernandez-Ayon, D. Ianson and B. Hales (2008). Evidence for upwelling of corrosive “acidified” water onto the continental shelf. *Science* 320:1490–92.
 53. Feely, R. A., J. Orr, V.J. Fabry, J.A. Kleypas, C.L. Sabine, and C. Landgon (2009). Present and future changes in seawater chemistry due to ocean acidification. In *Carbon Sequestration and Its Role in the Global Carbon Cycle*, Brian J. McPherson and Eric T. Sundquist (eds.), AGU Monograph.
 54. Feely, R. & Co-Authors (2010). "An International Observational Network for Ocean Acidification" in these proceedings (Vol. 2), doi:10.5270/OceanObs09.cwp.29.
 55. Feng, Y., M. E. Warner, Y. Zhang, J. Sun, F.-X. Fu, J. M. Rose and D. A. Hutchins (2008). Interactive effects of pCO₂, temperature and irradiance on the marine coccolithophore *Emiliana huxleyi* (Prymnesiophyceae), *European J. Phycology* 43, 87-98.
 56. Findlay, H. S., H. L. Wood, M. A. Kendall, J.I. Spicer, R. J. Twitchett and S. Widdicombe (2009). Calcification, a physiological process to be considered in the context of the whole organism, *Biogeosciences Discuss.* 6, 2267–2284, 2009, www.biogeosciences-discuss.net/6/2267/2009/.
 57. Fiorini, S., J. Middelburg and J.-P. Gattuso (2010). Seawater carbonate chemistry and biological processes during experiments with haploid and diploid life stages of *Emiliana huxleyi*, *Calcidiscus leptopus* and *Syracosphaera pulchra*, *J. Phycology* in press.
 58. Frankignoulle, M., C. Canon and J.-P. Gattuso (1994). Marine calcification as a source of carbon dioxide: positive feedback of increasing atmospheric CO₂, *Limnology and Oceanography* 39, 458-462.
 59. Fu, F.-X., M. E. Warner, Y. Zhang, Y. Feng and D. A. Hutchins (2007). Effects of increased temperature and CO₂ on photosynthesis, growth and elemental ratios of marine *Synechococcus* and *Prochlorococcus* (cyanobacteria), *J. Phycology* 43, 485-96.
 60. Gao, K. and Zheng, Y., (2010). Combined effects of ocean acidification and solar UV radiation on

- photosynthesis, growth, pigmentation and calcification of the coralline alga *Corallina sessilis* (Rhodophyta), *Global Change Biology* 16: 2388–2398.
61. Gao, K. S., Z. X. Ruan, V. E. Villafañe, et al. (2009). Ocean acidification exacerbates the effect of UV radiation on the calcifying phytoplankton *Emiliana huxleyi*, *Limnol. Oceanogr.* 54, 1855–1962.
 62. Garcia, H. E., T. P. Boyer, S. Levitus, R. A. Locarnini and J. I. Antonov (2005). Climatological annual cycle of upper ocean oxygen content anomaly. *Geophys. Res. Lett.* 32, L09604, doi:10.1029/2004GL022286.
 63. Gattuso, J.-P., M. Frankignoulle, I. Bourge, S. Romaine and R. W. Buddemeier (1998). Effect of calcium carbonate saturation of seawater on coral calcification, *Global and Planetary Change* 18, 37–46.
 64. Gazeau, F., C. Quiblier, J. M. Jansen, J.-P. Gattuso, J. J. Middelburg and C. H. R. Heip (2007). Impact of elevated CO₂ on shellfish calcification. *Geophys Res Lett* 34, L07603, doi:10.1029/2006GL028554.
 65. Gehlen, M., R. Gangstø, B. Schneider, L. Bopp, O. Aumont and C. Ethe (2007). The fate of pelagic CaCO₃ production in a high CO₂ ocean: a model study, *Biogeosciences* 4, 505–519, www.biogeosciences.net/4/505/2007/.
 66. Gooding, R. A., C. D. G. Harvey and E. Tang (2009). Elevated water temperature and carbon dioxide concentration increase the growth of a keystone echinoderm, *PNAS* 106, 316–9, 321.
 67. Green, M. A., M. E. Jones, C. L. Boudreau, R. L. Moore and B. A. Westman (2004). Dissolution mortality of juvenile bivalves in coastal marine deposits, *Limnol. Oceanogr.* 49, 727–734.
 68. Greenfield, D. I., R. Marin III, S. Jensen, E. Massion, B. Roman, J. Feldman and C. Scholin (2006). Application of the Environmental Sample Processor (ESP) methodology for quantifying *Pseudonitzschia australis* using ribosomal RNA-targeted probes in sandwich and fluorescent in situ hybridization, *Limnol. Oceanogr.*, *Methods* 4, 426–435.
 69. Greenfield, D., R. Marin III, G. J. Doucette, C. Mikulski, S. Jensen, B. Roman, N. Alvarado, and C. A. Scholin (2008). Field applications of the second-generation Environmental Sample Processor (ESP) for remote detection of harmful algae: 2006–2007, *Limnol. Oceanogr.*, *Methods* 6, 667–679.
 70. Gruber, N. & Co-Authors (2010). "Towards an Integrated Observing System for Ocean Carbon and Biogeochemistry at a Time of Change" in these proceedings (Vol. 1), doi:10.5270/OceanObs09.pp.18.
 71. Gruber, N. & Co-Authors (2010). "Adding Oxygen to Argo: Developing a Global In Situ Observatory for Ocean Deoxygenation and Biogeochemistry" in these proceedings (Vol. 2), doi:10.5270/OceanObs09.cwp.39.
 72. Guinotte J. M., R. W. Buddemeier and J. A. Kleypas (2003). Future coral reef habitat marginality: temporal and spatial effects of climate change in the Pacific basin. *Coral Reefs* 22, 551–8.
 73. Guinotte, J. M., J. Orr, S. Cairns, A. Freiwald, L. Morgan and R. George (2006). Will human induced changes in seawater chemistry alter the distribution of deep-sea scleractinian corals? *Front Ecol Environ* 4, 141–146.
 74. Gypens, N., A. V. Borges and C. Lancelot (2009). Effect of eutrophication on air-sea CO₂ fluxes in the coastal Southern North Sea: a model study of the past 50 years, *Global Change Biology* 15, 1040–1056.
 75. Hall-Spencer, J. M., R. Rodolfo-Metalpa, S. Martin, E. Ransome, M. Fine, S. M. Turner, S. J. Rowley, D. Tedesco and M. C. Buia (2008). Volcanic carbon dioxide vents show ecosystem effects of ocean acidification, *Nature* 454, 96–99, doi:10.1038/nature07051.
 76. Harris, J. O., G. B. Maguire, S. J. Edwards and M. Hindrum (1999). Effect of pH on growth rate, oxygen consumption rate, and histopathology of gill and kidney tissue for juvenile greenlip abalone, *Haliotis laevigata* Donovan and blacklip abalone, *Haliotis rubra* Leach, *J. Shellfish Research* 18, 611–619.
 77. Hauri, C., N. Gruber, G.-K. Plattner, S. Alin, R.A. Feely, B. Hales, and P.A. Wheeler (2009), Ocean acidification in the California Current System, *Oceanography* 22(4): 60–71.
 78. Havenhand, J. N. and P. Schlegel (2009). Near-future levels of ocean acidification do not affect sperm motility and fertilization kinetics in the oyster *Crassostrea gigas*, *Biogeosciences* 6, 3009–3015.
 79. Hollywood K, D. R. Brison and R. Goodacre (2006). Metabolomics: current technologies and future trends. *Proteomics* 6, 4716–4723.
 80. Hutchins, D. A., F.-X. Fu, Y. Zhang, M. E. Warner, Y. Feng, K. Portune, P. W. Bernhardt and M. R. Mulholland (2007). CO₂ control of *Trichodesmium* N₂ fixation, photosynthesis, growth rates, and elemental ratios: Implications for past, present, and future ocean biogeochemistry, *Limnol. Oceanogr.* 52, 1293–1304.
 81. Iglesias-Rodriguez, M. D., C. W. Brown, S. C. Doney, J. Kleypas, D. Kolber, Z. Kolber, P.K. Hayes and P. G. Falkowski (2002). Representing key phytoplankton functional groups in ocean carbon cycle models: Coccolithophorids. *Global Biogeochemical Cycles* 16, 1100, doi:10.1029/2001GB001454.
 82. Iglesias-Rodriguez, M. D., O. M. Schofield, J. Batley, L. K. Medlin and P. K. Hayes (2006). Intraspecific genetic diversity in the marine coccolithophorid *Emiliana huxleyi* (Prymnesiophyceae): the use of microsatellite analysis in marine phytoplankton population studies, *J. Phycol.* 42, 526–536.

83. Iglesias-Rodriguez M. D., P. R. Halloran, R. E. M. Rickaby, I. R. Hall, E. Colmenero-Hidalgo, J. R. Gittins, D. R. H. Green, T. Tyrrell, S. J. Gibbs, P. von Dassow, E. Rehm, V. E. Armbrust and K. P. Boessenkool (2008). Phytoplankton calcification in a high CO₂ world. *Science* 320, 336-39.
84. Ilyina, T., R. E. Zeebe, E. Maier-Reimer, C. Heinze (2009). Early detection of ocean acidification effects on marine calcification. *Global Biogeochemical Cycles* 23, GB1008, doi:10.1029/2008GB003278.
85. Invers, O., R. C. Zimmerman, R. S. Alberte, M. Perez and J. Romero (2001). Inorganic carbon sources for seagrass photosynthesis: an experimental evaluation of bicarbonate use in species inhabiting temperature waters, *J. Exp. Mar. Biol. Ecol.* 265: 203-217.
86. Jones G. P., M. I. McCormick, M. Srinivasan and J. V. Eagle (2004). Coral decline threatens fish biodiversity in marine reserves. *PNAS*, 101, 8251-8253.
87. Jonkers, L., F. Mienis, W. Boer, I. R. Hall and G.-J. A. Brummer (2010). Intra-annual variability of extremely rapid sedimentation onto Gardar Drift in the northern North Atlantic, *Deep-Sea Research I*, doi:10.1016/j.dsr.2010.05.005.
88. Joyce A. R. and B. Ø. Palsson (2006). The model organism as a system integrating 'omics' data sets. *Nature Rev Mol Cell Biol* 7, 198-210.
89. Kayanne, H., M. Yamamuro, H. Ohta et al. (2005). Seasonal and bleaching-induced changes in coral reef metabolism and CO₂ flux, *Glob. Biogeochem. Cycles* 19, GB3015, doi:10.1029/2004GB002400.
90. Keeling, C. D. (1965). Carbon dioxide in surface waters of the Pacific Ocean 2. Calculation of the exchange with the atmosphere, *Journal of Geophysical Research* 70, 6099-6102.
91. Keeling, R. F., A. Körtzinger and N. Gruber (2010). Ocean deoxygenation in a warming world, *Annu. Rev. Mar. Sci.* 2, 199-229.
92. Kendall, M. S., C. R. Kruer, K. R. Buja, J. D. Christensen, E. Diaz, R. A. Warner and M. E. Monaco (2004). A characterization of the shallow-water coral reefs and associated habitats of Puerto Rico, *Gulf and Caribbean Research* 16, 177-184.
93. Key, R. M., A. Kozyr, C. L. Sabine, K. Lee, R. Wanninkhof, J. L. Bullister, R. A. Feely, F. J. Millero, C. Mordy and T.-H. Peng (2004). A global ocean carbon climatology: Results from Global Data Analysis Project (GLODAP), *Global Biogeochemical Cycles* 18, GB4031, doi:10.1029/2004GB002247.
94. Kleypas, J. A., R. W. Buddemeier, D. Archer, J.-P. Gattuso, C. Langdon and B. N. Opdyke (1999). Geochemical consequences of increased atmospheric carbon dioxide on coral reefs, *Science* 284, 118-120.
95. Kleypas, J. A., R. W. Buddemeier and J.-P. Gattuso (2001). The future of coral reefs in an age of global change, *Int. J. Earth Sci.* 90, 426-437.
96. Kleypas, J. A., R. A. Feely, V. J. Fabry, C. Langdon, C. L. Sabine and L. L. Robbins (2006). Impacts of ocean acidification on coral reefs and other marine calcifiers: a guide for future research, report of a workshop held 18-20 April 2005, St. Petersburg, FL, sponsored by NSF, NOAA, and the US geological Survey. http://www.ucar.edu/communications/Final_acidification.pdf.
97. Kranz, S. A., D. Sültemayer and B. Rost (2009). Carbon acquisition by *Trichodesmium*: the effect of pCO₂ and diurnal changes, *Limnol. Oceanogr.* 54, 548-559.
98. Kuffner, I. B., A. J. Anderson, P. L. Jokiel, K. S. Rodgers and F. T. Mackenzie (2008). Decreased abundance of crustose coralline algae due to ocean acidification, *Nat. Geosci.* 1, 77-140.
99. Kurihara, H. and Y. Shirayama (2004). Effects of increased atmospheric CO₂ on sea urchin early development *Mar Ecol Prog Ser* 274, 161-169.
100. Kurihara, H., S. Shimode and Y. Shirayama (2004). Effects of raised CO₂ concentration on the egg production rate and early development of two marine copepods (*Acartia steueri* and *Acartia erythraea*). *Marine Pollution Bulletin* 49, 721-727.
101. Langdon, C. and M. J. Atkinson (2005). Effect of elevated pCO₂ on photosynthesis and calcification of corals and interactions with seasonal change in temperature/irradiance and nutrient enrichment. *J. Geophysical Res.* 110, 2005, C09S07, doi:10.1029/2004JC002576.
102. Langdon, C., T. Takahashi, C. Sweeney, D. Chipman, J. Goddard et al. (2000). Effect of calcium carbonate saturation state on the calcification rate of an experimental coral reef, *Glob. Biogeochem. Cycles* 14, 639-54.
103. Langdon, C., W. S. Broecker, D.E. Hammond, E. Glenn, K. Fitzsimmons, S. G. Nelson, T.-S. Peng, I. Hajdas and G. Bonani (2003). Effect of elevated CO₂ on the community metabolism of an experimental coral reef. *Global Biogeochemical Cycles* 17, doi:10.1029/2002GB001941.
104. Langer, G., M. Geisen, K.-H. Baumann, J. Kläs, U. Riebesell, S. Thoms and J. R. Young (2006). Species-specific responses of calcifying algae to changing seawater carbonate chemistry, *G-cubed* 7, Q09006, doi:10.1029/2005GC001227.
105. Langer, G., G. Nehrke, I. Probert, J. Ly and P. Ziveri (2009). Strain specific responses of *Emiliania huxleyi* to changing seawater carbonate chemistry, *Biogeosciences* 6, 2637-2646, <http://www.biogeosciences.net/6/2637/2009/>.
106. Lebrato, M., M. D. Iglesias-Rodriguez, R. A. Feely, D. Greeley, D. Jones, N. E. Suarez-Bosche, R. S. Lampitt, J. Cartes, D. R. H. Green, and B. Alker (2009). Global contribution of echinoderms to the marine carbon cycle: a re-assessment of the oceanic CaCO₃ budget and the benthic compartments.

107. Leclercq, N., J.-P. Gattuso and J. Jaubert (2002). Primary production, respiration, and calcification of a coral reef mesocosm under increased CO₂ partial pressure. *Limnology and Oceanography* 47, 558–564.
108. Lefevre, N., J. P. Ciabrini, G. Michard, B. Briant, M. DuChaffaut and L. Merlivat (1993). A new optical sensor for pCO₂ measurements in seawater, *Mar. Chem.* 42, 189–198.
109. Levitan, O., G. Rosenberg, I. Setlik, E. Setlikova, J. Grigel, J. Klepetar, O. Prasil and I. Berman-Frank (2007). Elevated CO₂ enhances nitrogen fixation and growth in the marine cyanobacterium *Trichodesmium*, *Global Change Biology* 13, 531–538.
110. Lindinger, M. I., D. J. Laurén and D. G. McDonald (1984). Acid-base balance in the sea mussel, *Mytilus edulis*. III. Effects of environmental hypercapnia on intra- and extracellular acid-base balance, *Mar. Biol. Lett.* 5, 371–381.
111. Mackenzie F. T., A. Lerman and A. J. Andersson (2004). Past and present of sediment and carbon biogeochemical cycling models. *Biogeosciences* 1, 27_85. <http://www.biogeosciences.net/bgd/1/27/>.
112. Metzger, R., F. J. Sartoris, M. Langenbuch and H. O. Pörtner (2007). Influence of elevated CO₂ concentrations on thermal tolerance of the edible crab *Cancer pagurus*, *J. Therm. Biol.* 32, 144–151.
113. Michaelidis, B., C. Ouzounis, A. Palaras and H. O. Pörtner (2005). Seawater carbonate chemistry and processes during experiments with marine mussel *Mytilus edulis*, *Mytilus galloprovincialis*, *Mar. Ecol. Prog. Ser.* 293, 109–118.
114. Miles, H., S. Widdicombe, J. I. Spicer and J. Hall-Spencer (2007). Effects of anthropogenic seawater acidification on acid-base balance in the sea urchin *Psammechinus miliaris*, *Mar. Pollut. Bull.* 54, 89–96.
115. Monaco, M. E., A. M. Friedlander, C. Caldow, J. D. Christensen, C. Rogers, J. Beets, J. Miller and R. Boulon (2007). Characterizing reef fish populations and habitats within and outside the U.S. Virgin Islands Coral Reef National Monument: a lesson in marine protected area design, *Fisheries Management and Ecology* 14, 33–40.
116. Morse, J. W., A. J. Andersson, F. T. Mackenzie. 2006. Initial responses of carbonate-rich shelf 1369 sediments to rising atmospheric PCO₂ and “ocean acidification”: role of high Mg-calcites. 1370 *Geochimica et Cosmochimica Acta* 70, 5814–5830.
117. Moy, A. D., W. R. Howard, S. G. Bray and T. W. Trull (2009). Reduced calcification in modern Southern Ocean planktonic foraminifera, *Nature Geoscience* 2, 276 - 280, doi:10.1038/ngeo460.
118. Müller, M. N., K. G. Schulz and U. Riebesell (2010). Effects of long-term high CO₂ exposure on two species of coccolithophores, *Biogeosciences* 7, 1109–1116.
119. Nienhuis, S., A. R. Palmer and C. D. Harley (2010). Elevated CO₂ affects shell dissolution rate but not calcification rate in a marine snail. *Proceedings of the Royal Society B: Biological Sciences* doi:10.1098/rspb.2010.0206.
120. Omar, A., T. Johannessen, S. Kaltin and A. Olsen (2003). Anthropogenic increase of oceanic pCO₂ in the Barents Sea surface water, *J. Geophys. Res.* 108(C12), 3388, doi:10.1029/2002JC001628.
121. Orr J. C., V. J. Fabry, O. Aumont, L. Bopp, S. C. Doney, et al. (2005). Anthropogenic ocean acidification over the twenty-first century and its impact on calcifying organisms. *Nature* 437, 681–86.
122. Oschlies, A., K. G. Schulz, U. Riebesell and A. Schmittner (2008). Simulated 21st century’s increase in oceanic suboxia by CO₂-enhanced biotic carbon export, *Global Biogeochemical Cycles* 22, GB4008, doi:10.1029/2007GB003147.
123. Palacios, S. L. and R. C. Zimmerman (2007). Response of eelgrass *Zostera marina* to CO₂ enrichment: possible impacts of climate change and potential for remediation of coastal habitats, *Mar Ecol Prog Ser* 344: 1–13.
124. Pörtner, H. O. and A. Reipschläger (1996). In Ormerod, B., Angel, M. (eds), *Ocean storage of CO₂. Environmental Impact*. MIT and International Energy Agency, Boston/Cheltenham, 57–81.
125. Reynaud S., N. Leclercq, S. Romaine-Lioud, C. Ferrier-Pages, J. Jaubert, J.-P. Gattuso (2003). Interacting effects of CO₂ partial pressure and temperature on photosynthesis and calcification in a scleractinian coral. *Glob. Chang. Biol.* 9, 1660–68.
126. Rickaby, R. E. M., J. Henderiks and J. N. Young (2010). Perturbing phytoplankton: a tale of isotopic fractionation in two coccolithophore species, *Clim. Past Discuss.* 6, 257–294.
127. Ridgwell, A. and D. N. Schmidt (2010). Past constraints on the vulnerability of marine calcifiers to massive carbon dioxide release, *Nature Geoscience* 3, 196 - 200.
128. Riebesell U, I. Zondervan, B. Rost, P. D. Tortell, R. E. Zeebe and F. M. M. Morel (2000). Reduced calcification of marine plankton in response to increased atmospheric CO₂, *Nature* 407, 364–67.
129. Riebesell, U., A. Körtzinger and A. Oschlies (2009). Tipping Elements in Earth Systems Special Feature: Sensitivities of marine carbon fluxes to ocean change. *Proceedings of the National Academy of Sciences* 106: 49, 20602–20609.
130. Riebesell U., V. J. Fabry, L. Hansson and J.-P. Gattuso (Eds.), 2010. *Guide to best practices in ocean acidification research and data reporting*, 264 p. Luxembourg: Office for Official Publications of the European Communities.

131. Ries, J. B., A. L. Cohen and D. C. McCorkle (2009). Marine calcifiers exhibit mixed responses to CO₂-induced ocean acidification, *Geology* 37, 1131-1134; doi:10.1130/G30210A.1.
132. Rodolfo-Metalpa, R., S. Martin, C. Ferrier-Pages and J.-P. Gattuso (2010). Response of the temperate coral *Cladocora caespitosa* to mid- and long-term exposure to pCO₂ and temperature levels projected for the year 2100 AD. *Biogeosciences* 7, 289-300.
133. Rosa, R. and B. A. Seibel (2008). Synergistic effects of climate-related variables suggest future physiological impairment in a top oceanic predator, *PNAS* 105, 20776-20780.
134. Sabine, C. L., R. A. Feely, N. Gruber, R. M. Key, K. Lee, J. L. Bullister, R. Wanninkhof, C. S. Wong, D. W. R. Wallace, B. Tilbrook, F. J. Millero, T.-H. Peng, A. Kozyr, T. Ono and A. F. Rios (2004). The Oceanic Sink for Anthropogenic CO₂, *Science* 305, 367 - 371, doi:10.1126/science.1097403.
135. Sabine C. L. and R. A. Feely (2007). The oceanic sink for carbon dioxide. In *Greenhouse Gas Sinks*, ed. D Reay, N, Hewitt, J Grace, K Smith, pp. 31-49. Oxfordshire: CABI Publishing.
136. Salisbury, J. E., D. Vandemark, C. W. Hunt, J. W. Campbell, W. R. McGillis, and W. H. McDowell (2008), Seasonal observations of surface waters in two Gulf of Maine estuary-plume systems: Relationships between watershed attributes, optical measurements and surface pCO₂, *Estuarine Coastal Shelf Sci.*, 77, 245-252.
137. Santana-Casiano, J. M., M. Gonzalez-Davila, M. J. Rueda, O. Llinas and E. F. Gonzalez-Davila, E.F. (2007). The interannual variability of oceanic CO₂ parameters in the northeast Atlantic subtropical gyre at the ESTOC site, *Global Biogeochemical Cycles* 21, GB1015. doi:10.1029/2006GB002788.
138. Schlueter, M. and T. Gentz (2008). Application of membrane inlet mass spectrometry for online and in situ analysis of methane in aquatic environments, *J. Am. Soc. Mass Spectrom.*, 19, 1395-1402.
139. Scholin, C. A., G. J. Doucette and A. D. Cembella (2008). Prospects for developing automated systems for in situ detection of harmful algae and their toxins, in: *Real-Time Coastal Observing Systems for Ecosystem Dynamics and Harmful Algal Blooms*, edited by: Babin, M., Roesler, C. S., and Cullen, J. J., UNESCO Publishing, Paris, France, 413-462.
140. Seidel, M. P., M. D. DeGrandpre and A. G. Dickson (2008), A sensor for in situ indicator-based measurements of seawater pH, *Mar. Chem.* 109, 18-28.
141. Shi, D., Y. Xu and F. M. M. Morel (2009), Effects of the pH/pCO₂ control method on medium chemistry and phytoplankton growth, *Biogeosciences* 6, 1199-1207.
142. Shi, D., Y. Xu, B. M. Hopkinson and F. M. M. Morel (2010). Effect of ocean acidification on iron availability to marine phytoplankton. *Science* 327, 676-679.
143. Short, F. T. and H. A. Neckles (1999). The effects of global climate change on seagrasses, *Aquatic Botany* 63, 169-196.
144. Silverman, J., B. Lazar, L. Cao, K. Caldeira and J. Erez (2009). Coral reefs may start dissolving when atmospheric CO₂ double, *Geophysical Research Letters* 36, L05606, doi:10.1029/2008GL036282.
145. Sogin M. L., H. G. Morrison, J. A. Huber, D. M. Welch, S. M. Huse, P. R. Neal, J. M. Arrieta, G. J. Herndl (2006). Microbial diversity in the deep sea and the underexplored 'rare biosphere', *Proc Natl Acad Sci USA* 103, 12115-12120.
146. Spero, H., J. Bijma, D. W. Lea and E. B. Bemis (1997). Seawater carbonate chemistry and carbon and oxygen isotopes during experiments with planktonic foraminifera *Orbulina universa* and *Globigerina bulloides*, *Nature* 390, 497-500.
147. Steinacher, M., F. Joos, T. L. Frölicher, G.-K. Plattner and S. C. Doney (2009). Imminent ocean acidification in the Arctic projected with the NCAR global coupled carbon cycle-climate model *Biogeosciences* 6, 515-533, www.biogeosciences.net/6/515/2009/.
148. Thomas, H., A. E. F. Prowe, S. van Heuven, Y. Bozec, H. J. W. de Baar, L.-S. Schiettecatte, K. Suykens, M. Kone, A.V. Borges, I. D. Lima and S. C. Doney (2007). Rapid decline of the CO₂ buffering capacity in the North Sea and implications for the North Atlantic Ocean, *Global Biogeochemical Cycles* 21, GB4001, doi:10.1029/2006GB002825.
149. Tortell, P.D., G. H. Rau and F. M. M. Morel (2000). Inorganic carbon acquisition in coastal Pacific phytoplankton communities. *Limnol Oceanogr* 45, 1485-1500.
150. Tortell, P. D., G. R. DiTullio, D. M. Sigman and F. M. M. Morel (2002). CO₂ effects on taxonomic composition and nutrient utilization in an Equatorial Pacific phytoplankton assemblage, *Mar Ecol Prog Ser* 236, 37-43.
151. Tortell, P. D., C. D. Payne, Y. Li, S. Trimborn, B. Rost, W. O. Smith, C. Riesselman, R. B. Dunbar, P. Sedwick, G. R. DiTullio (2008). CO₂ sensitivity of Southern Ocean phytoplankton, *Geophysical Research Letters* 35, L04605, 5 PP., doi:10.1029/2007GL032583.
152. Turley C., M. Eby, A. J. Ridgwell, D. N. Schmidt, H. S. Findlay, C. Brownlee, U. Riebesel, J.-P. Gattuso, V. J. Fabry, R. A. Feely. (2010) The societal challenge of ocean acidification. *Marine Pollution Bulletin*, 60, 787-792.
153. Venter, J. C., K. Remington, J. F. Heidelberg, A. L. Halpern, D. Rusch, J. A. Eisen, D. Wu, I. Paulsen, K. E. Nelson, W. Nelson, D. E. Fouts, S. Levy, A. H. Knap, M. W. Lomas, K. Nealson, O. White, J. Peterson, J. Hoffman, R. Parsons, H. Baden-Tillson,

- C. Pfannkoch, Y.-H. Rogers and H. O. Smith (2004). Environmental Genome Shotgun Sequencing of the Sargasso Sea, *Science* 304, 66–74, doi:10.1126/science.1093857.
154. Wallace, D. W. R. (2001). Storage and transport of excess CO₂ in the oceans: The JGOFS/WOCE global CO₂ survey (2001), in: *Ocean Circulation and Climate*, edited by G. Siedler, J. Church, and J. Gould, Elsevier, New York, pp. 489-521.
155. Walther, K., F. J. Sartoris, C. Bock and H. O. Pörtner (2009). Impact of anthropogenic ocean acidification on thermal tolerance of the spider crab *Hyas araneus*, *Biogeosciences* 6, 2207–2215.
156. Watson, A. J., U. Schuster, D. C. E. Bakker, N. R. Bates, A. Corbière, M. González-Dávila, T. Friedrich, J. Hauck, C. Heinze, T. Johannessen, A. Körtzinger, N. Metzl, J. Olafsson, A. Olsen, A. Oschlies, X. A. Padin, B. Pfeil, J. M. Santana-Casiano, T. Steinhoff, M. Telszewski, A. F. Rios, D. W. R. Wallace and R. Wanninkhof (2009). Tracking the variable North Atlantic sink for atmospheric CO₂, *Science* 326, 1391–1393, doi:10.1126/science.1177394.
157. Wenner, P. G., R. J. Bell, F. H. W. van Amerom, S. K. Toler, J. E. Edkins, M. L. Hall, K. Koehn, R. T. Short and R. H. Byrne (2004). Environmental chemical mapping using an underwater mass spectrometer, *Trends in Anal. Chem.*, Special issue on deploying mass spectrometers in harsh environments 23, 288–295.
158. Wood, H. L., J. I. Spicer and S. Widdicombe (2008). Ocean acidification may increase calcification rates, but at a cost, *Proc. R. Soc. B* 275, 1767–1773. doi:10.1098/rspb.2008.0343.
159. Yamada, Y. and T. Ikeda (1999). Acute toxicity of lowered pH to some oceanic zooplankton, *Plankton Biology and Ecology* 46, 62-67.
160. Yamamoto-Kawai, M., F. A. McLaughlin, E. C. Carmack, S. Nishino and K. Shimada, Aragonite undersaturation in the Arctic Ocean: effects of ocean acidification and sea ice melt, *Science* 20, 326 1098–1100, doi:10.1126/science.1174190.
161. Zachos, J.C., G.R. Dickens and R.E. Zeebe (2008). An early Cenozoic perspective on greenhouse warming and carbon-cycle dynamic, *Nature* 451: 279-283.
162. Zimmerman, R.C., Kohrs, D.G., Steller, D.L. and Alberte, R.S., 1997, Impacts of CO₂ Enrichment on Productivity and Light Requirements of Eelgrass, *Plant Physiology* 115,599-607.
163. Zondervan, I., R. E. Zeebe, B. Rost and U. Riebesell (2001). Decreasing marine biogenic calcification: a negative feedback on rising atmospheric pCO₂. *Global Biogeochem. Cycles* 15, 507–516.
164. Zondervan, I., B. Rost and U. Riebesell (2002). Effect of CO₂ concentration on the PIC/POC ratio in the coccolithophore *Emiliana huxleyi* grown under light-limiting conditions and different day lengths, *Journal of Experimental Marine Biology and Ecology* 272, 55– 70.