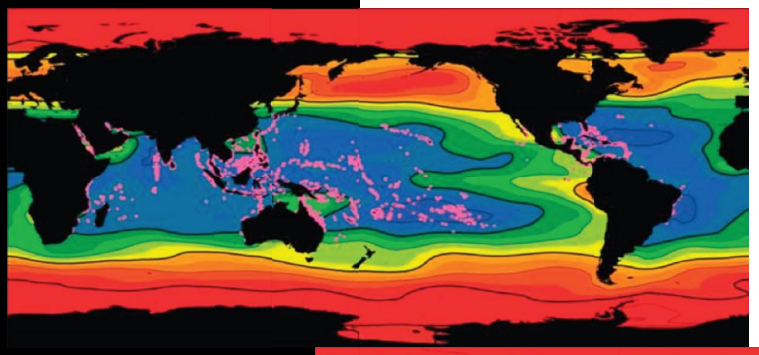
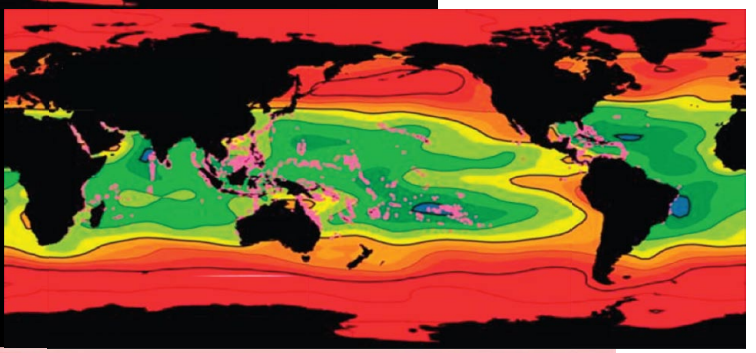
Secretariat of the Convention on Biological Diversity

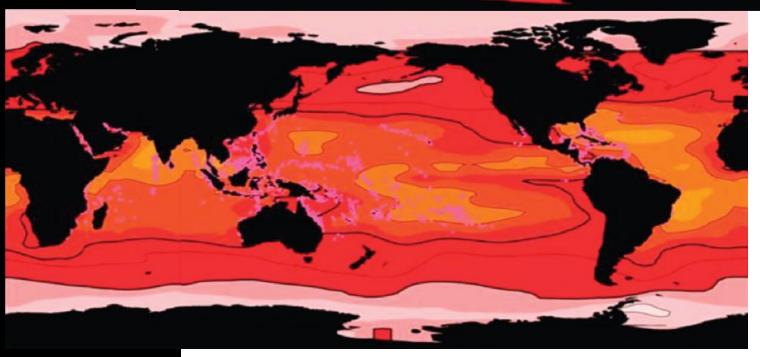
CBD Technical Series No. 46

46

Scientific Synthesis of the Impacts of Ocean Acidification on Marine Biodiversity







Convention on Biological Diversity

UNEP

WCMC

CBD Technical Series No. 46

Scientific Synthesis of the Impacts of Ocean Acidification on Marine Biodiversity

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Front cover: Maps of aragonite saturation state at increasing atmospheric carbon dioxide (CO_2) stabilization concentrations. The value in each of the scenarios is derived from the year used for each CO_2 stabilization pathway in the described model, i.e. top: pre-industrial (280ppm in 1765), middle: present-day (380ppm in 2010*), and bottom: a future projection (750ppm in 2250). The year 2250 is derived from the extrapolation that the pathway will increase by 50ppm every 25 years starting from 450ppm in 2100.

* atmospheric CO_2 concentrations are currently 387 ppm (2009)

Credits: Maps: Cao, L and Caldeira, K. (2008). Atmospheric CO_2 stabilization and ocean acidification, *Geophysical Research Letters* 35:L19609, pp. 5. Photograph: Jason Hall-Spencer *et al.* 2008

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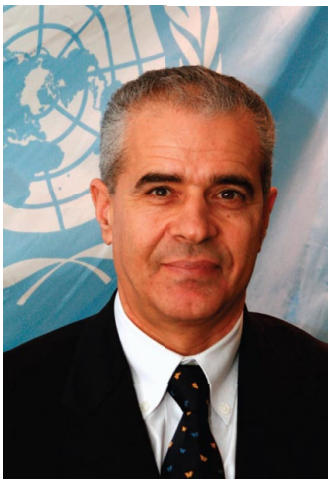
FOREWORD



Over the past decade, the Conference of the Parties (COP) to the CBD has consistently raised its concerns about the threats of climate change on biodiversity and provided relevant policy guidance. As a result, significant efforts have been made to raise awareness of the adverse impacts of climate change on biodiversity and the significant role of biodiversity in climate change adaptation and mitigation.

At its fourth meeting, in 1998, the COP expressed its deep concern over the extensive and severe coral bleaching occurring at that time and noted that this event was a possible consequence of global warming. At its fifth meeting, in 2000, the COP urged the UN Framework Convention on Climate Change (UNFCCC) to take all possible actions to reduce the effect of climate change on water temperatures and to address the socio-economic impacts on the countries and communities most affected by coral bleaching.

Recently, in its ninth meeting, the COP raised its concerns about the potential impacts of ocean acidification, a direct consequence of increasing atmospheric CO_2 concentrations, occurring independently of climate change. This publication was prepared as a direct response to a request made by COP 9 to compile and synthesize available scientific information on ocean acidification and its impacts on marine biodiversity and habitats, which is identified as a potentially serious threat to cold-water corals and other marine biodiversity.

Among others findings, this study shows that increasing ocean acidification reduces the availability of carbonate minerals in seawater, important building blocks for marine plants and animals, and that by 2100, 70% of cold-water corals, key refuges and feeding grounds for commercial fish species, will be exposed to corrosive waters. Furthermore, given current emission rates, it is predicted that the surface waters of the highly productive Arctic Ocean will become under-saturated with respect to essential carbonate minerals by the year 2032, and the Southern Ocean by 2050, with disruptions to large components of the marine food web.

This initial effort, produced jointly with the UNEP World Conservation Monitoring Centre (UNEP-WCMC), confirms that there is an urgent need to establish a joint expert process within the CBD, in collaboration with other relevant UN/international organizations, to monitor and assess the impacts of ocean acidification on marine and coastal biodiversity, and to raise the awareness of policy-makers on its possible ecological and socio-economic implications, with a view of promoting a joint work programme between the two sister Rio Conventions, UNFCCC and CBD.

Dr. Ahmed Djoghlaf
Executive Secretary
Convention on Biological Diversity

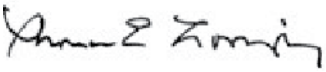
PREFACE

In 1980, I wrote in the foreword for *Conservation Biology,* by Michael Soulé and Bruce Wilcox, that *"hundreds of thousands of species will perish, and this reduction of 10 to 20 percent of the earth's biota will occur in about half a human life span....This reduction of the biological diversity of the planet is the most basic issue of our time."* That thought was not echoed by the global community and policy-makers until the Convention on Biological Diversity (CBD) entered into force in 1993.

After 16 years of implementation of the Convention and with less than a month to achieve the 2010 biodiversity targets, the basic issue of our time, biodiversity, has nonetheless yet to reach the heart of every global citizen. Moreover, it is now eclipsed by global debates on climate change that largely ignore that the planet works as a biophysical system. As a consequence, far too many policy-makers at the 2009 UN Climate Change Conference in Copenhagen seem unaware that biological diversity not only underpins and is at the heart of global sustainable development, it is also being threatened gravely by climate change. Understanding the role of biodiversity in attaining our common goal of sustainability is therefore not only critical, but urgent.

In this regard, this publication by the CBD on the impacts of ocean acidification on marine biodiversity is very timely and germane, as it confirms again how great the stakes of sustainability are in the climate change negotiations. It is sadly still true, and ever more evident, that we are in deep trouble biologically and heading into a spasm of extinction of our own making unequalled since the one which took the dinosaurs. It is not an exaggeration to highlight again that the rate at which species disappear is about 1,000 to 10,000 times normal, and a quarter or more of all species could vanish within a couple of decades. Biological diversity must be at the centre of any discussion on sustainability and efforts for climate change mitigation and adaptation.

Therefore, this scientific synthesis by the CBD Secretariat and the UNEP-World Conservation Monitoring Centre (WCMC) is especially valuable. It is expected that a continuing effort be made within CBD, in collaboration with relevant international organizations and scientific communities, to build upon this publication, further enhancing scientific research on ocean acidification, particularly its biological and biogeochemical consequences, including the accurate determination of sub-critical levels of impacts or tipping points for global marine species, ecosystems and the services and functions they provide.



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The Secretariat of the Convention on Biological Diversity would like to thank Nicola Barnard and Stefan Hain from UNEP-WCMC for conducting the research and preparing this report in the CBD Technical Series. The Secretariat wishes to acknowledge with appreciation the generous funding received from Government of Spain, which made this study possible, as well as the funding from the UNEP-WCMC, which contributed to the publication of the report. The Secretariat would also like to express its appreciation to Brazil, New Zealand, Norway, Thailand, USA, Vietnam, Greenpeace International, Elva Escobar, William R Howard, Jean-Pierra Gattuso, Francine Kershaw, Suzanne R Livingstone, Hine - Wai Loose and Kristian Teleki for providing information and valuable comments to improve this report. Gratitude is also expressed to the Secretariat staff who contributed to the editing of the report.

EXECUTIVE SUMMARY

The surface ocean plays a critical role in the global carbon cycle, absorbing approximately one quarter of the carbon dioxide emitted to the atmosphere from the burning of fossil fuels, deforestation, and other human activities. As more and more anthropogenic CO_2 has been emitted into the atmosphere, the ocean has absorbed greater amounts at increasingly rapid rates. In the absence of this service by the oceans, atmospheric CO_2 levels would be significantly higher than at present and the effects of global climate change more marked.

The absorption of atmospheric CO_2 has, however, resulted in changes to the chemical balance of the oceans (which are naturally slightly alkaline), causing them to become more acidic. Ocean acidity has increased significantly, by 30%, since the beginning of the Industrial Revolution 250 years ago.

Atmospheric CO_2 concentrations are predicted to increase by 0.5%-1.0% per year throughout the 21st century. Ocean acidification directly follows the accelerating trend in world CO_2 emissions, and the magnitude of ocean acidification can be ascertained with a high level of certainty based on the predictable marine carbonate chemistry reactions and cycles within the ocean. It is predicted that by 2050 ocean acidity could increase by 150%. This significant increase is 100 times faster than any change in acidity experienced in the marine environment over the last 20 million years, giving little time for evolutionary adaptation within biological systems.

Increasing ocean acidification reduces the availability of carbonate minerals in seawater, important building blocks for marine plants and animals. Carbonate ion concentrations are now lower than at any other time during the last 800,000 years. Furthermore, given current emission rates, it is predicted that the surface waters of the highly productive Arctic Ocean will become under-saturated with respect to essential carbonate minerals by the year 2032, and the Southern Ocean by 2050 with disruptions to large components of the marine food web. Seasonal fluctuations in carbonate mineral saturation in the Southern Ocean could mean that detrimental conditions for the continuing function of marine ecosystems, especially calcifying organisms, develop on much shorter timeframes.

It has been predicted that by 2100, 70% of cold-water corals, key refuges and feeding grounds for commercial fish species, will be exposed to corrosive waters. Tropical waters, such as those around the Great Barrier Reef, will also experience rapid declines in carbonate ions, reducing rates of net warm water coral reef accretion and leaving biologically diverse reefs outpaced by bioerosion and sea-level rise.

An emerging body of research suggests that many of the effects of ocean acidification on marine organisms and ecosystems will be variable and complex, impacting developmental and adult phases differently across species depending on genetics, pre-adaptive mechanisms, and synergistic environmental factors. Evidence from naturally acidified locations confirms, however, that although some species may benefit, biological communities under acidified seawater conditions are less diverse and calcifying species absent.

Many questions remain regarding the biological and biogeochemical consequences of ocean acidification for marine biodiversity and ecosystems, and the impacts of these changes on oceanic ecosystems and the services they provide, for example, in fisheries, coastal protection, tourism, carbon sequestration and climate regulation. In order to accurately predict the consequences, the ecological effects must be considered alongside other environmental changes associated with global climate change.

Ocean acidification is irreversible on timescales of at least tens of thousands of years, and substantial damage to ocean ecosystems can only be avoided by urgent and rapid reductions in global emissions of CO_2, and the recognition and integration of this critical issue in the global climate change debate.

I. BACKGROUND AND INTRODUCTION

Rising atmospheric carbon dioxide (CO_2) concentrations, driven by fossil fuel combustion, cement manufacturing and deforestation, among other activities, have led to greater CO_2 uptake by oceanic surface waters. The inorganic carbon system is an important chemical equilibrium in the ocean and is largely responsible for controlling the pH of seawater[1]. Consequently, the oceanic uptake of CO_2, which accounts for approximately one-quarter to one-third of the CO_2 released from all human activities into the atmosphere since 1800, has resulted in changes to the chemical balance of seawater and a reduction in pH, termed "ocean acidification"[2, 3]

Ocean acidification is an observable and predictable consequence of increasing atmospheric CO_2 concentrations[4] now and in the future, given the well-known physio-chemical pathways and reactions of CO_2 as it dissolves in seawater. However, given the nascent recognition of ocean acidification as a global threat, the resulting impacts on marine species and ecosystem processes are still poorly understood[5]. The predicted consequences for marine plants and animals, food security and human health are profound, including disruption to fundamental biogeochemical processes, regulatory ocean cycles, marine food chains and production, and ecosystem structure and function[6, 7].

In 2008, 155 scientists from 26 countries gathered for the second International Symposium on the Ocean in a High CO_2 World, signed a declaration (The Monaco Declaration) as a message to global leaders urging action to mitigate the already detectable effects of ocean acidification, and cautioning against the rapid and widespread predicted costs of inaction for the continued provision of ocean goods and services[8]. In 2009, the Inter-Academy Panel on International Issues (IAP) released a statement on ocean acidification, endorsed by 70 of the world's leading scientific academies, calling for ocean acidification to be considered in the international climate change debate, and recommending the urgent reduction of global emissions of CO_2 by at least 50% by 2050 to stabilise temperature increases and acidification at sub-critical levels[9]. Ocean acidification has also been the subject of other institutional reviews and syntheses worldwide[10].

Ocean acidification research is still in its infancy, and many questions remain about its biological and biogeochemical consequences, and the accurate determination of sub critical levels, or "tipping points" for global marine species, ecosystems and services. In particular, most understanding of biological impacts due to ocean acidification is derived from studies of individual organism responses. There is a critical need for information on impacts at the ecosystem level (e.g. changes in species composition, community-level production and calcification). In its decision IX/20 (marine and coastal biodiversity), the

1 Fabry, V. J., Seibel, B. A., Feely, R. A., Orr, J. C. (2008). Impacts of ocean acidification on marine fauna and ecosystem processes. ICES Journal of Marine Science, 65:414–432.

2 Doney, S. C., Fabry, V. J., Feely, R. A., Kleypas, J. A. (2009). Ocean Acidification: The Other CO_2 problem. Annu. Rev. Mar. Sci. 1:169–192.

3 Canadell *et al.*, 2007: Contributions to accelerating atmospheric CO_2 growth from economic activity, carbon intensity, and efficiency of natural sinks, in Proceedings of the National Academy of Science 104:47:18866–18870, doi: 10.1073/pnas.0702737104

4 Doney, S. C., Fabry, V. J., Feely, R. A., Kleypas, J. A. (2009). Ocean Acidification: The Other CO_2 problem. Annu. Rev. Mar. Sci. 1:169–192

5 Kleypas, J. A., Buddemeier, R. W., Archer, D., Gattuso, J. P., Langdon, C., Opdyke, B. N. (1999). Geochemical Consequences of Increased Atmospheric Carbon Dioxide on Coral Reefs. Science, Vol 284:118–120.

6 EUR-OCEANS. (2007). Fact Sheet 7: Ocean Acidification – the other half of the CO_2 problem. www.eur-oceans.eu/KTU

7 GC(52)/INF/3 (2008). Nuclear Technology Review 2008.

8 Monaco Declaration. Second International Symposium on the Ocean in a High-CO_2 World, Monaco, October 2008. http://ioc3.unesco.org/oanet/Symposium2008/MonacoDeclaration.pdf)

9 Inter-Academy Panel on International Issues (IAP). 2009. Statement on Ocean Acidification. Endorsed, June 2009. www.interacademies.net/CMS/9075.aspx

10 Hobart Communiqué on Ocean Acidification: Australian Impacts in the Global Context, Antarctic Climate & Ecosystems Cooperative Research Centre, Hobart, Tasmania, Workshop Report 2–4 June 2008; Royal Society of New Zealand, (2009), Ocean Acidification: Emerging Issues, 4 pp, Wellington, New Zealand, www.royalsociety.org.nz/includes/download.aspx?ID=102240

Conference of the Parties to the Convention on Biological Diversity "*... requests the Executive Secretary, in collaboration with Parties, other Governments, and relevant organizations, to compile and synthesize available scientific information on ocean acidification and its impacts on marine biodiversity and habitats, which is identified as a potentially serious threat to cold-water corals and other marine biodiversity, and to make such information available for consideration at a future meeting of the Subsidiary Body on Scientific, Technical and Technological Advice (SBSTTA) prior to the tenth meeting of the Conference of Parties.*"[11]

A. OBJECTIVES OF THE REPORT

This report presents a review and synthesis of existing literature and other scientific information on the potential impacts of ocean acidification on marine biodiversity pursuant to decision IX/20. The report takes into consideration comments and feedbacks submitted by Parties, other Governments and organizations as well as experts who kindly peer-reviewed the report.

In accordance with the requirements set out in decision IX/20, the outputs of this work shall be submitted for consideration as an information document to SBSTTA 14, scheduled for May 2010.

The research for this report was conducted in collaboration with the UNEP World Conservation Monitoring Centre (UNEP-WCMC), with the kind financial support of the Government of Spain.

CARBON AND CO_2 UNIT CONVERSION TABLE

Climate change mitigation measures often refer to the natural uptake or engineered capture and storage of carbon (C), while in the context of greenhouse gas emissions it is referred to the gaseous form of carbon, carbon dioxide (CO_2). The relation between the two is as follows:

1 tonne of carbon corresponds to **3.67 tonnes of carbon dioxide**

In this report, tonnes are metric tonnes (i.e. 10^6 grams), and total carbon stores are provided in gigatonnes of carbon (Gt C) and stores per area in tonnes of carbon per m^2 (t C m^2). Carbon fluxes are presented in tonnes of carbon per year (t C per yr) or tonnes of carbon per m^2 per year (t C m^2 per yr).

1 Gt C of carbon corresponds to **10^9 t C.**

B. DEFINITION(S) OF OCEAN ACIDIFICATION

The measure used to define the acidity of a solution is pH units. On this logarithmic scale, a decrease of 1 unit corresponds to a 10-fold increase in the concentration of Hydrogen (H^+) ions and represents significant acidification. Currently, the surface waters of the oceans are slightly alkaline, with an overall mean pH of ~8.1 on the seawater scale, approximately 0.1 pH units less than the estimated preindustrial values[12].

The dissolution of CO_2 into the oceans increases the concentration of H^+ ions, which reduces pH, making the oceans more acidic. It is important to note that the pH of the oceans is currently greater than pH=7 (neutral pH), and thus the term "ocean acidification" refers to the oceans becoming progressively less basic along the pH scale (see Fig 1).

11 see http://www.cbd.int/decision/cop/?id=11663, accessed 10 May 2009

12 Feely, R. A., Doney, S. C., and S.R. Cooley (2009), Ocean Acidification: Present conditions and future changes in a high-CO_2 world, Oceanography, submitted for publication.

In 2007, the Intergovernmental Panel on Climate Change (IPCC) defined ocean acidification as "*A decrease in the pH of sea water due to the uptake of anthropogenic carbon dioxide.*"[13]

There are numerous more detailed definitions and descriptions (see also section C below) of the term ocean acidification in the scientific literature, including:

> "*... The addition of carbon dioxide in seawater that causes a reduction in ocean pH and shifts in carbonate speciation*", with pH defined as "*a measure of ocean acidity and hydrogen ion H+ concentration; pH = −log10[H+]*" [14]
>
> "*...Oceanic uptake of CO_2 drives the carbonate system to lower pH and lower saturation states of the carbonate minerals calcite, aragonite, and high-magnesium calcite, the materials used to form supporting skeletal structures in many major groups of marine organisms. ...*"[15]

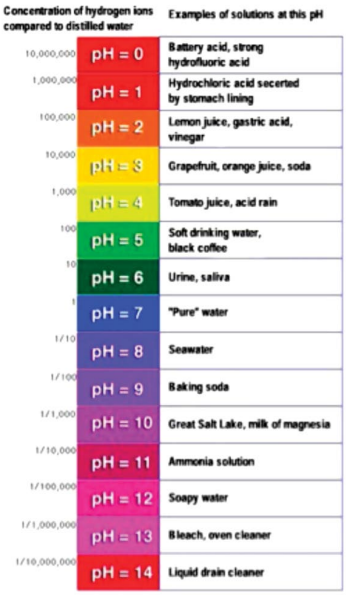


FIGURE 1: The pH scale. *Source: US Environmental Protection Agency*

C. SCIENTIFIC DESCRIPTION OF OCEAN ACIDIFICATION

The ocean is one of the largest natural reservoirs of carbon, with an estimated daily uptake of 22 million metric tons of CO_2[16]. Gases are readily exchanged across the air-sea interface due to differences in the partial pressure of CO_2 (pCO_2) between the ocean and the atmosphere, making the oceans of considerable importance in the global carbon cycle[17]. There are important interactions and feedbacks between changes in the state of the oceans and changes in the global climate and atmospheric chemistry, which can influence the ability of the oceans to absorb additional CO_2 from the atmosphere, affecting the rate and scale of global climate change[18].

Solubility and Distribution of CO_2 in the Oceans

The solubility and distribution of CO_2 in the oceans depends on climatic conditions and a number of physical (e.g. water column mixing, temperature), chemical (e.g. carbonate chemistry) and biological (e.g. biological productivity) factors. For example, the uptake of CO_2 by marine algae during photosynthesis creates a deficit of CO_2 in surface ocean waters, driving the dissolution of CO_2 from the atmosphere into the surface ocean to restore the equilibrium[19]. Figure 2 shows the calculated mean annual sea-air CO_2 flux, with yellow-red colours indicating a net release of $C0_2$ to the atmosphere, and blue-purple colours indicating a net up-take of CO_2 from the atmosphere.

13 IPCC (2007) Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change. Cambridge University Press: Cambridge, UK and New York, NY, USA

14 Doney, S. C., Fabry, V. J., Feely, R. A., Kleypas, J. A. (2009). Ocean Acidification: The Other CO_2 problem. Annu. Rev. Mar. Sci. 1:169–192.

15 Kleypas, J. A., Feely, R. A., Fabry, V. J., Langdon, C., Sabine, C. L., Robbins, L. L. (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 U.S Geological Survey, 88 pp.

16 Feely, R. A., Sabine, C. L., Hernandez-Ayon, J. M., Lanson, D., Hales, B. (2008). Evidence for Upwelling of Corrosive "Acidified" Water onto the Continental Shelf. Science, Vol320:1490 -1492.

17 The Royal Society (2005). Ocean Acidification due to increasing atmospheric carbon dioxide. Policy Document 12/05. http://royalsociety.org/document.asp?id=3249

18 The Royal Society (2005). Ocean Acidification due to increasing atmospheric carbon dioxide. Policy Document 12/05. http://royalsociety.org/document.asp?id=3249

19 Chisholm, S. W. (2000). Stirring times in the Southern Ocean. Nature. Vol 407. 12 October 2000.

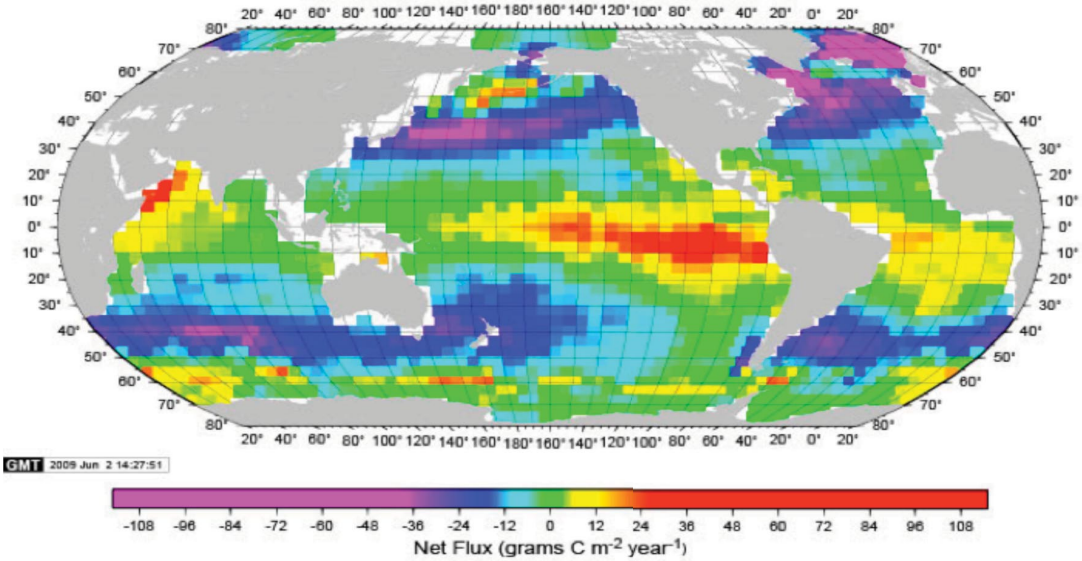


FIGURE 2: Mean Annual Air-Sea CO_2 Flux for 2000 (Revised June 2009). *Source: http://www.ldeo.columbia.edu/res/pi/CO2/carbondioxide/pages/air_sea_flux_2000.html based on Takahashi,* et al. *2009*[20].
A climatic mean distribution for the surface water pCO_2 over the global oceans in non-El Niño conditions are presented with spatial resolution of 4° (latitude) x 5° (longitude) for a reference year 2000 based upon 3.0 million measurements of surface water pCO_2 obtained from 1970 to 2007. Wind speed data from the 1979–2005 NCEP-DOE AMIP-II Reanalysis and the gas transfer coefficient with a scaling factor of 0.26. The annual mean for the contemporary net CO_2 uptake flux over the global oceans is estimated to be -1.4 ± 0.7 Pg-C/yr. Taking the pre-industrial steady state ocean source of 0.4 ± 0.2 Pg-C/yr into account, the total ocean uptake flux including the anthropogenic CO_2 is estimated to be –2.0 ± 0.7 Pg-C/yr in 2000.

Once CO_2 has been absorbed into surface waters, it is transported horizontally and vertically to the deep ocean by a suite of biologically and physically mediated processes. In addition to advection and mixing the ocean can alter atmospheric CO_2 concentration through three basic mechanisms: the "solubility pump", the "organic carbon pump" and the "$CaCO_3$ counter pump"—the latter two are often summarized as the "biological pump" (Figure 3)[21].

Biological Pump: The "organic carbon pump" (biological pump) is driven by the primary production of marine phytoplankton, which converts dissolved inorganic carbon (DIC) (the sum of bicarbonate ions, undissociated $CO_{2\,(aq)}$ and carbonate ions)[22], and nutrients into organic matter through photosynthesis[23]. This process is limited by the availability of light and nutrients, for example, phosphate, nitrate and silicic acid, and micronutrients, such as iron. The uptake of CO_2 through photosynthesis prompts the "drawdown" of additional CO_2 from the atmosphere, fuels the flux of sinking particulate organic carbon into the deep ocean as organisms die or are consumed, and drives global marine food webs. This cycle maintains a vertical gradient in the concentration of DIC, with higher values at depth and lower values at the surface[24].

20 Takahashi, T., S. C. Sutherland, R. Wanninkhof, C. Sweeney, R. A. Feely, D. W. Chipman, B. Hales, G. Friederich, F. Chavez, A. Watson, D. C. E. Bakker, U. Schuster, N. Metzl, H. Yoshikawa-Inoue, M. Ishii, T. Midorikawa, Y. Nojiri, C. Sabine, J. Olafsson, Th. S. Arnarson, B. Tilbrook, T. Johannessen, A. Olsen, Richard Bellerby, A. Körtzinger, T. Steinhoff, M. Hoppema, H. J. W. de Baar, C. S. Wong, Bruno Delille and N. R. Bates (2009). Climatological mean and decadal changes in surface ocean pCO_2, and net sea-air CO_2 flux over the global oceans. Deep-Sea Res. II, 56, 554–577

21 IPCC (2007) Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change. Cambridge University Press: Cambridge, UK and New York, NY, USA

22 Le Queré, C. and Metzl, N. (2004). Natural Processes Regulating the Ocean Uptake of CO_2. In: The Global Carbon Cycle: Integrating Humans, Climate, and the Natural World. (C. B. Field and M. R. Raupach, Eds.) Island Press: Washington, D.C., USA. pp. 243–255

23 Ibid.

24 Hofmann, M. and Schellnhuber, H. J. (2009). Ocean acidification affects marine carbon pump and triggers extended marine oxygen holes. PNAS 106, 3017–3022.

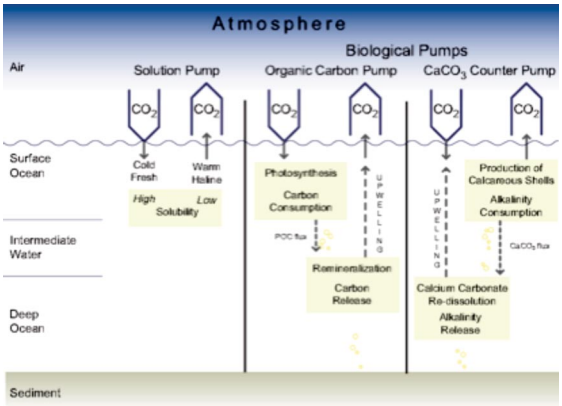


FIGURE 3: Three main ocean carbon pumps govern the regulation of natural atmospheric CO_2 changes by the ocean. *Source: Denman, K.L* et al. *(2007). Couplings Between Changes in the Climate System and Biogeochemistry. In:* Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change *[Solomon, S.,* et al. *(eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA (redrawn after Heinze, C., E. Maier-Reimer, and K. Winn, 1991: Glacial /p/CO2 reduction by the World Ocean: experiments with the Hamburg carbon cycle model* Paleoceanography *6(4), 395–430.)*

Although most of the CO_2 taken up by phytoplankton is recycled near the surface, a substantial fraction, perhaps 30%, sinks into the deeper waters before being converted back (remineralized) into CO_2 by marine bacteria. Only about 0.1% reaches the seafloor to be buried in the sediments[25]. Of note, the removal of CO_2 via primary production increases surface water pH, whereas adding CO_2 via respiration decreases pH, leading to an observed diurnal variation in pH within highly productive systems[26].

Solubility Pump: In addition to the absorption or release of CO_2 due to biological processes, changes in the solubility of gaseous CO_2 can alter CO_2 concentrations in the oceans and the overlying atmosphere. The solubility pump reflects the temperature dependence of the solubility of CO_2 (i.e. solubility is greater in colder water) and the thermal stratification of the ocean[27]. The solubility pump is another important mechanism for controlling the inventory of carbon in the ocean. Large-scale thermohaline circulation is driven by the formation of deep water at high latitudes, where cold, dense waters sink and flow into the deep ocean basins. Since these deep water masses are formed under the same surface conditions that promote carbon dioxide solubility, they contain a high concentration of DIC, accumulated at the surface, which is transported to the deeper parts of the oceans as the water mass sinks.

Large-scale ocean circulation processes slowly transport CO_2-rich bottom waters over long distances from the Atlantic to the Indian and Pacific oceans, which accumulate further DIC as they travel. As such, concentrations of DIC are approximately 10–15% higher in deep waters than at the surface, and lower in the Atlantic than the Indian Ocean, with the highest concentrations found in the older deep waters of the North Pacific Ocean. Figure 4 shows the mean pre-industrial distribution of dissolved inorganic carbon along north-south transects in the Atlantic, Indian and Pacific oceans. Figure 5 shows the estimated mean distributions of anthropogenic CO_2 concentrations along the same transects.

Data-based estimates indicate that globally, the oceans have accumulated 112 (±17)[28] petagrams of Carbon (Pg C) since the beginning of the industrial era, or 118 (±19)[29] Pg C between 1800 – 1994, corresponding to an uptake of about 29% of the total CO_2 emissions from burning fossil fuels, land use change and cement production, among other activities, within the last 250 years[30, 31]. The observed annual

25 Feely, R. A., Sabine, L., Takahashi, T., Wanninkhof, R. (2001). Uptake and Storage of Carbon Dioxide in the Ocean: The Global CO_2 Survey. Oceanography, Vol. 14(4): pp. 18–32

26 Raven, J.A., Falkowski, P.G. (1999) Oceanic sinks for atmospheric CO_2. Plant, Cell and Environment. Vol 22. pp. 741–755

27 Ito, T., Follows, M. J. (2003). Upper ocean control on the solubility pump of CO_2. Journal of Marine Research, 61:485–489.

28 Lee, *et al.* (2003). An updated anthropogenic CO_2 inventory in the Atlantic Ocean. Global Biogeochemical Cycles 17, 1116

29 Sabine, C. L., Freely, R. A., Gruber, N., Key, R. M., Lee, K., Bullister, J. L., *et al.* (2004). The oceanic sink for CO_2. Science, 305:367–371.

30 Lee, *et al.* (2003). An updated anthropogenic CO_2 inventory in the Atlantic Ocean. Global Biogeochemical Cycles 17, 1116

31 Sabine, C. L., Feely, R. A., Gruber, N., Key, R. M., Lee, K., Bullister, J. L., *et al.* (2004). The oceanic sink for CO_2. Science, 305:367–371.

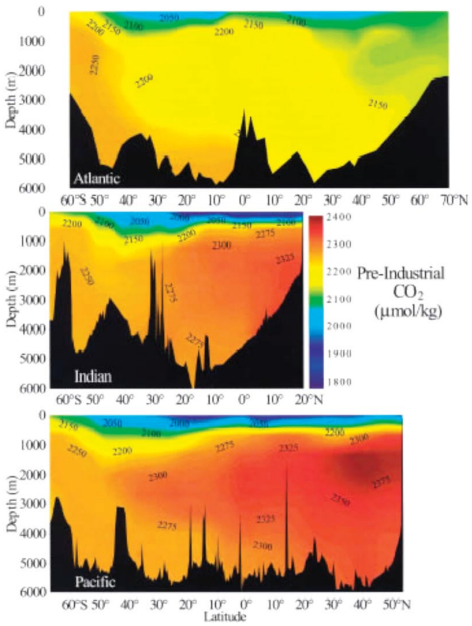


FIGURE 4: Zonal mean pre-industrial distributions of dissolved inorganic carbon (in units of µmol kg) along north-south transects in the Atlantic, Indian and Pacific ocean. S*ource: Feely, R. A., Sabine, L., Takahashi, T., Wanninkhof, R. (2001). Uptake and Storage of Carbon Dioxide in the Ocean: The Global CO_2 Survey.* Oceanography *14(4): pp. 18–32.*

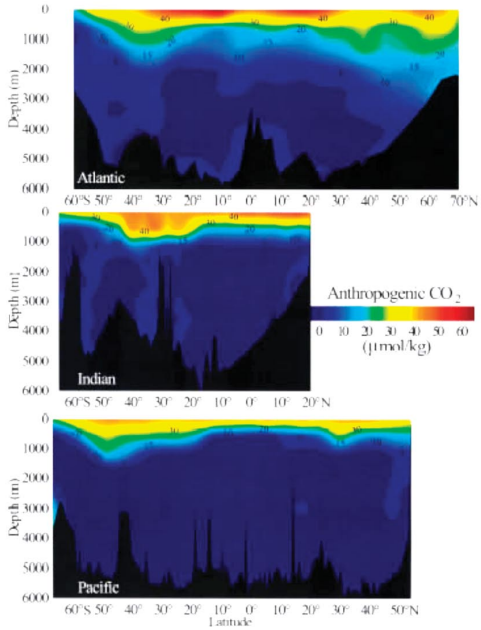


FIGURE 5: Zonal mean distributions of estimated anthropogenic CO_2 concentrations (in units of µmol kg) along north-south transects in the Atlantic, Indian and Pacific ocean. S*ource: Feely, R. A., Sabine, L., Takahashi, T., Wanninkhof, R. (2001). Uptake and Storage of Carbon Dioxide in the Ocean: The Global CO_2 Survey.* Oceanography *14(4): pp. 18–32.*

uptake of anthropogenic CO_2 by the ocean for the period 1990 – 1999 of 2.2 (±0.4) Pg C yr^{-1}, led to an estimate that the ocean sink accounted for 24% of total anthropogenic emissions from 2000 – 2006[32].

The deepest penetrations of this anthropogenic carbon are observed in areas of deep and intermediate water formation, such as the North Atlantic, and the Southern Ocean, 40–50°S. Figure 5 shows that the anthropogenic CO_2 signal can be found in depths of up to 2500m in certain areas, although newer studies in the North Atlantic have revealed large changes in CO_2 concentrations in deep-water masses between 3,000 and 5,000 metres depth, indicating that the CO_2 signal might already have penetrated to this depth in certain locations[33].

Depending on the location and ocean currents, CO_2 can be retained in deep waters for several hundred (up to a 1,000) years[34, 35]. This means that the equivalent CO_2 content is temporarily removed (sequestered) from the atmosphere for this time period. Wind- or topography-driven upwelling of deep ocean waters brings DIC-laden waters back to the surface, often resulting in an efflux of CO_2 to the atmosphere.

32 Canadell *et al.*, 2007: Contributions to accelerating atmospheric CO_2 growth from economic activity, carbon intensity, and efficiency of natural sinks, in Proceedings of the National Academy of Science 104:47:18866–18870, doi: 10.1073/pnas.0702737104

33 Tanhua, T., Körtzinger, A., Friis, K., Waugh, Wallace, D.W.R. (2007). An estimate of anthropogenic CO_2 inventory from decadal changes in oceanic carbon content. Proceedings of the National Academy of Sciences. Vol. 104 (9). pp. 3037–3042

34 IPCC (2005): IPCC Special Report on Carbon Dioxide Capture and Storage. Prepared by Working Group III of the Intergovernmental Panel on Climate Change [Metz, B., O. Davidson, H. C. de Coninck, M. Loos, and L. A. Meyer (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 442 pp

35 Chisholm, S. W. (2000). Oceanography: Stirring times in the Southern Ocean. Nature 407. pp. 685–687

The solubility pump has been estimated to contribute about 20% to the vertical distribution/gradient of DIC; the remaining 80% originates from the biological pump(s)[36]. It should be noted that increasing sea-surface temperatures as a result of climate change will decrease the solubility of CO_2. Different climate models predict ocean temperature increases throughout this century[37], which means that less CO_2 will be absorbed at the surface. Model outcomes suggest that the strength of the solubility pump is highly correlated with mean surface and deep-ocean temperatures[38]. In the long term, the solubility of CO_2 may decrease, or in the worst-case, even interrupt, the ocean's solubility pump. A more sluggish ocean circulation and increased density stratification, both expected in a warmer climate, would slow down the vertical transport of carbon, alkalinity and nutrients, and the replenishment of the ocean surface with water that has not yet been in contact with anthropogenic CO_2[39]. This would seriously influence the ocean's carbon uptake capacity.

One study suggests that while both land and ocean sinks continue to accumulate carbon on average at ~5.0± 0.6 Pg C y^{-1} since 2000, large regional sinks have been weakening. In the Southern Ocean for example, the sink of CO_2 has weakened by 0.8 Pg C yr^{-1} between 1981 and 2004[40]. The poleward displacement and intensification of westerly winds caused by human activities is thought to have enhanced the ventilation of carbon-rich waters in the Southern Ocean, which, since at least 1980, are normally isolated from the atmosphere, contributing nearly half of the decrease in the ocean CO_2 uptake fraction estimated through modelling[41]. A rapid decline of the CO_2 buffering capacity is also reported from the North Sea[42].

Ocean Carbonate System

In seawater, CO_2 molecules are present in four major forms: the undissociated form ($CO_{2\,(aq)}$) and carbonic acid (H_2CO_3), and two ionic forms, bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) (see Table 1 and Figure 6). The proportion of each of these carbon components in seawater is sensitive to temperature, chemical composition and pressure, and thus to latitude and depth, creating a varied carbonate chemistry response to CO_2 uptake across the oceans[43]. The difference between the partial pressure of CO_2 (pCO_2) in surface seawater and that in the overlying air represents the thermodynamic driving potential for the CO_2 transfer across the sea surface[44, 45].

When CO_2 dissolves in surface seawater it reacts with water to form a weak carbonic acid (H_2CO_3).

$$CO_2 + H_2O \leftrightarrow H_2CO_3$$

36 Feely, R. A., Sabine, L., Takahashi, T., Wanninkhof, R. (2001). Uptake and Storage of Carbon Dioxide in the Ocean: The Global CO_2 Survey. Oceanography, Vol. 14(4): pp. 18–32

37 Matthews, H. D. and Caldeira, K. (2008). Stabilizing climate requires near-zero emissions. Geophysical Research Letters 35, L04705

38 Cameron, D. R., Lenton, T. M., Ridgwell, A. J., Shepherd, J. G., Marsh, R., and Yool, A. (2005). A factorial analysis of the marine carbon cycle and oceanic circulation controls on atmospheric CO_2. Global Biogeochemical Cycles 19, GB4027

39 IPCC (2007) Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change. Cambridge University Press: Cambridge, UK and New York, NY, USA

40 Le Quéré, Corinne, Rodenbeck, Christian, Buitenhuis, Erik T., Conway, Thomas J., Langenfelds, Ray, Gomez, Antony, Labuschagne, Casper, Ramonet, Michel, Nakazawa, Takakiyo, Metzl, Nicolas, Gillett, Nathan, and Heimann, Martin (2007). Saturation of the Southern Ocean CO_2 Sink Due to Recent Climate Change. Science 1136188.

41 Canadell *et al.*, 2007: Contributions to accelerating atmospheric CO_2 growth from economic activity, carbon intensity, and efficiency of natural sinks, in Proceedings of the National Academy of Science 104:47:18866–18870, doi: 10.1073/pnas.0702737104

42 Thomas, H., Prowe, A. E. F., van Heuven, S., Bozec, Y., De Baar, H. J. W., Schiettecatte, L.-S., Suykens, K., Koné, M., Borges, A. V., Lima, I. D., and Doney, S. C. (2007). Rapid decline in CO_2 buffering capacity in the North Sea and implications for the North Atlantic Ocean. Global Biogeochemical Cycles 21, GB4001.

43 Veron, J. E. N. (2008) Mass extinctions and ocean acidification: biological constraints on geological dilemmas. Coral Reefs 27:459–472.

44 Feely, R. A., Sabine, C. L., Takahashi, T., Wanninkof, R. (2001). Uptake and storage of Carbon Dioxide in the Ocean: The Global CO_2 Survey. Special Issue – JGOFS, Oceanograhpy Vol 14 (4).

45 Sabine, C. L., Feely, R. A., Gruber, N., Key, R. M., Lee, K., Bullister, J. L., *et al.* (2004). The oceanic sink for CO_2. Science, 305:367–371.

Carbonic acid dissociates into bicarbonate ions (HCO_3^-) and hydrogen ions (H^+). The release of hydrogen ions decreases the pH (i.e. increases the acidity) of surrounding waters.

$$H_2CO_3 \leftrightarrow HCO_3^- + H^+$$

Excess hydrogen ions (H^+) react with carbonate ions (CO_3^{2-}) to form further bicarbonate ions.

$$H^+ + CO_3^{2-} \leftrightarrow HCO_3^-$$

The acidity of the oceans is determined by the concentration of hydrogen ions; a greater amount results in more acidic conditions, represented by a lower pH.

The amount of CO_2 that dissolves into surface seawater will therefore strongly influence the acidity and pH of the oceans[46]. In line with Henry's law[47], an increase in atmospheric CO_2 concentrations from, for example, anthropogenic emissions, will lead to a corresponding increase in the pCO_2 in the surface ocean[48].

The ratio of ions HCO_3^-, CO_3^{2-} and CO_2 in seawater in relation to pH is shown in Table 1. Under current ocean conditions, bicarbonate is the most abundant form of CO_2 dissolved in seawater. Increased CO_2 absorption in the surface ocean will increase both bicarbonate and hydrogen ion concentrations, and concurrently lower the availability of carbonate ions[49], which are necessary for calcium carbonate ($CaCO_3$) skeleton and shell formation in marine organisms such as corals, shellfish and marine plankton[50].

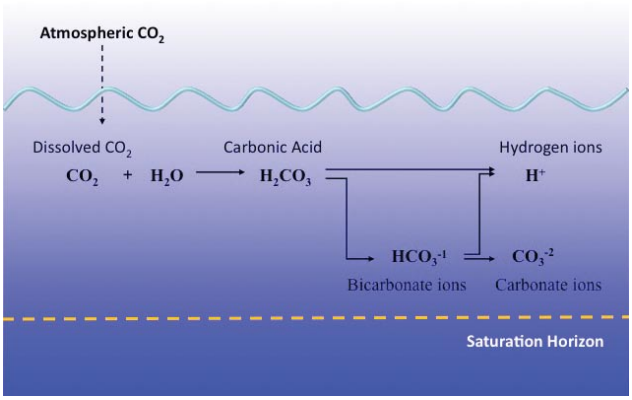


FIGURE 6: The reaction of CO_2 and seawater. *Source: Adapted from Doney, 2006*[51].

46 The Royal Society (2005). Ocean Acidification due to increasing atmospheric carbon dioxide. Policy Document 12/05. http://royalsociety.org/document.asp?id=3249

47 Henry's law states that "*at a constant temperature, the amount of a given gas dissolved in a given type and volume of liquid is directly proportional to the partial pressure of that gas in equilibrium with that liquid*".

48 The Royal Society (2005). Ocean Acidification due to increasing atmospheric carbon dioxide. Policy Document 12/05. http://royalsociety.org/document.asp?id=3249

49 The Antarctic Climate and Ecosystems Cooperative Research Centre. (2008). Position Analysis: CO_2 and climate change: ocean impacts and adaptation issues. www.acecrc.org.au/uploaded/117/797618_20pa02_acidification_0805.pdf.

50 Feely, R. A., Sabine, C. L., Hernandez-Ayon, J. M., Lanson, D., Hales, B. (2008). Evidence for Upwelling of Corrosive "Acidified" Water onto the Continental Shelf. Science, Vol320:1490 -1492.

51 Doney, S. C. (2006). The Dangers of Ocean Acidification. Scientific American March 2006. www.sciam.com

TABLE 1. Forms of dissolved inorganic carbon (DIC) in seawater.

Dissolved inorganic carbon (DIC) in seawater		Component % of DIC at pH 8.2[55].	Component % of DIC at pH 8.1[56]	Net effect of adding CO_2 in surface waters on DIC component
Bicarbonate ion	HCO_3^-	88	91	Increase
Carbonate ion	CO_3^{2-}	11	8	Decrease
Aqueous carbon dioxide (including H_2CO_3)	$CO_{2(aq)}$	0.5	1.0	Increase

Mineralization and Dissolution of Calcium Carbonate

The "$CaCO_3$ counter pump describes the effects of the production and dissolution of calcium carbonate materials (e.g. calcareous shells of planktonic organisms) on the alkalinity and pH of seawater. As described above, the $CaCO_3$ counter pump and organic carbon pump (biological pump), in conjunction with the solubility pump, are ways in which the ocean exerts an influence on atmospheric CO_2 concentrations (see Figure 3)[54]. The main chemical reactions for the mineral formation and the dissolution of calcium carbonate ($CaCO_3$) are as follows:

$$CaCO_3^- \leftrightarrow Ca^{2+} + CO_3^{2-}$$

$$CaCO_3 + H_2O + CO_2^- \leftrightarrow Ca^{2+} + 2HCO_3^-$$

Calcium carbonate is formed from right to left, and dissolved from left to right. Calcification and dissolution affect both DIC and the ability of seawater to neutralize acids (total alkalinity (A_T)). On a global scale, $CaCO_3$ plays a dual role in regulating carbon sequestration by the oceans. The equilibrium between $CaCO_3$ precipitation and dissolution processes is influenced by CO_2 concentrations in surface waters[55]. The precipitation of $CaCO_3$ in the upper ocean, through the formation of calcareous skeletons by marine organisms, creates less alkaline conditions, which decreases the capacity of the upper ocean to take up atmospheric CO_2[56], whereas a decrease in production in the upper ocean, or the dissolution of marine carbonates at depth, including biogenic magnesium calcites (from coralline algae), aragonite (from corals and pteropods), and calcite (from coccolithophorids and foraminifera), raises pH and increases the capacity of the oceans to take up and store CO_2 from the atmosphere[57]. Both reactions are temperature and pressure sensitive, which means that in warmer and shallower seas, the balance lies more towards the left (mineralization), whereas in deeper and colder seas, the balance is more to the right (dissolution). It should be noted that as much as 60–80% of the $CaCO_3$ exported from the surface layers may be dissolved in the upper 1000 metres of the water column[58].

52 Fabry, V. J., Seibel, B. A., Feely, R. A., Orr, J. C. (2008). Impacts of ocean acidification on marine fauna and ecosystem processes. ICES Journal of Marine Science, 65:414–432.

53 The Royal Society (2005). Ocean Acidification due to increasing atmospheric carbon dioxide. Policy Document 12/05. http://royalsociety.org/document.asp?id=3249

54 IPCC (2007) Climate Change 2007: The Physical Science Basis. (Chapter 7: Couplings between changes in the climate system and biogeochemistry) Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change. Cambridge University Press: Cambridge, UK and New York, NY, USA.

55 Kleypas, J. A., Buddemeier, R. W., Archer, D., Gattuso, J. P., Langdon, C., Opdyke, B. N. (1999). Geochemical Consequences of Increased Atmospheric Carbon Dioxide on Coral Reefs. Science, Vol 284:118–120.

56 Kleypas, J. A., Feely, R. A., Fabry, V. J., Langdon, C., Sabine, C. L., Robbins, L. L. (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 U.S Geological Survey, 88 pp.

57 Feely, R. A., Sabine, C. L., Lee, K., Berelson, W., Kleypas, J., Fabry, V. J., Millero, F. J. (2004). Impact of anthropogenic CO_2 on the $CaCO_3$ system in the oceans. Science, 305:362–365.

58 Ibid.

Carbonate Buffering

The reaction of CO_2 with seawater to form dissociated $CO_{2\,(aq)}$ and CO_3^{2-} and HCO_3^-, means that the resulting increase in gaseous seawater CO_2 concentration is smaller than the actual amount of CO_2 entering the seawater. This "chemical buffering" is quantitatively the most important oceanic process contributing to the ocean as a carbon sink[59], and maintains the slightly basic pH of seawater within relatively narrow limits, despite the uptake of atmospheric CO_2. The buffer function is not, however, a constant, and varies depending on, *inter alia*, changes in pCO_2 and the ratio of DIC to A_T. It is predicted that as the oceans' alkalinity decreases due to CO_2 uptake from the atmosphere, and surface pCO_2 increases, the capacity of the global oceans to buffer increasing atmospheric CO_2 will decline, with potentially severe consequences[60].

Calcium Carbonate ($CaCO_3$) Saturation Horizon

The carbonate buffering process is known to lower the degree of saturation of seawater ("saturation state (Ω)") with respect to carbonate minerals such as calcite and aragonite, which in turn affects the stability and production rates of these important building blocks[61, 62]. When seawater is supersaturated with aragonite and calcite ($\Omega>1$), as is the case in all ocean surface waters at present, the formation of shells and skeletons will be favoured. Conversely, when seawater is under saturated with respect to these minerals ($\Omega<1$) the seawater becomes corrosive and the shells of calcifying organisms are increasingly prone to dissolution[63]. $CaCO_3$ becomes more soluble with decreasing temperature and increasing pressure and therefore ocean depth, creating a natural boundary known as the "saturation horizon" above which $CaCO_3$ can form, but below which it readily dissolves[64]. The saturation horizon starts at a depth varying between 200 m in parts of the high-latitudes and the Indian Ocean, and 3,500 m in the Atlantic[65].

The depth of this saturation horizon ($\Omega=1$) for aragonite, a more soluble form of $CaCO_3$, is naturally significantly shallower than that for calcite, as demonstrated in Figure 7[66]. As CO_2 driven ocean acidity increases, carbonate ions are removed from the system in the carbonate buffering process (see above), and the saturation horizon shallows towards surface waters, termed "shoaling". The shoaling of these saturation horizons and subsequent dissolution of sedimentary carbonates is one of the major long-term buffering mechanisms by which the ocean's pH will be restored. However, this process operates over millennial time scales and will be processed only as anthropogenic CO_2 reaches the saturation depths through ocean circulation[67]. Shoaling of the saturation horizon reduces the habitat available for calcifying organisms reliant on the carbonate minerals and has implications for ecosystem productivity, function and the provision of services, especially for cold-, deep-water species such as cold-water corals.

59 IPCC (2007) Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change. Cambridge University Press: Cambridge, UK and New York, NY, USA

60 Ibid.

61 Zeebe, R. E., Zachos, J. C., Tyrrell, T. (2008) Carbon emissions and Acidification. Science Vol 321:51–52.

62 Fabry, V. J. (2008). Marine Calcifiers in a High-CO_2 Ocean. Science Vol 320:1020–1022.

63 Feely *et al* (1988). Mar. Chem. 25:227.

64 The Royal Society (2005). Ocean Acidification due to increasing atmospheric carbon dioxide. Policy Document 12/05. http://royalsociety.org/document.asp?id=3249

65 IPCC (2007) Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change. Cambridge University Press: Cambridge, UK and New York, NY, USA

66 Feely, R. A., Sabine, C. L., Lee, K., Berelson, W., Kleypas, J., Fabry, V. J., Millero, F. J. (2004). Impact of anthropogenic CO_2 on the $CaCO_3$ system in the oceans. Science, 305:362–365.

67 Montenegro *et al*, Brovkin, A., V., Eby, M., Archer, D., and Weaver, A. J. (2007), Long term fate of anthropogenic carbon, Geophys. Res. Lett., 34, L19707, doi:10.1029/2007GL030905

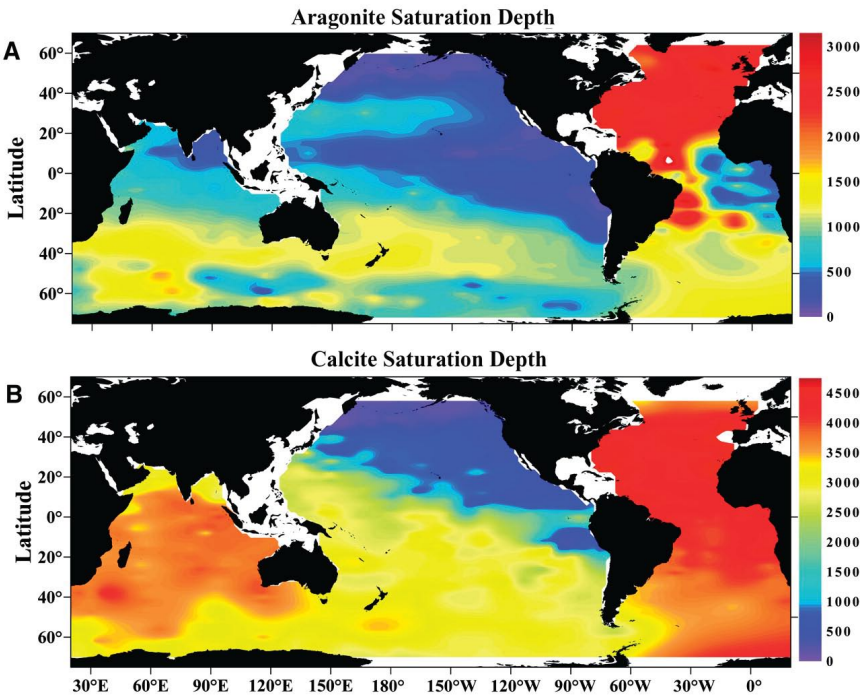


FIGURE 7: Distribution of (**A**) aragonite and (**B**) calcite saturation depth (Ω=1) in the global oceans. *Source: Feely* et al. *2004*[68]. The pressure effect on the solubility is estimated from the equation of Mucci[69] that includes the adjustments to the constants recommended by Millero[70]. The level at which aragonite and calcite are in thermodynamic equilibrium is known as the saturation depth. When the degree of saturation, , is greater than 1, seawater is supersaturated with aragonite and calcite; conversely, seawater is undersaturated with respect to these minerals when < 1. This depth is significantly shallower for aragonite than for calcite, because aragonite is more soluble in seawater than calcite.

Laboratory and field studies have observed that the degree of saturation has a profound effect on the calcification rates of species and communities in both planktonic and benthic habitats, as lower pH reduces the saturation of the seawater making calcification by marine organisms harder (more energy costly) and weakening structures that have been formed (see Section III). $CaCO_3$ makes calcifying organisms denser ("mineral ballast") and increases sinking rates of decomposing and dead particulate organic carbon. A reduction in calcification decreases the amount of ballast available for the sedimentation of organic matter and $CaCO_3$, which has implications for the biological pump and sequestration of carbon in the ocean interior[71].

68 Feely, R. A., Sabine, C. L., Lee, K., Berelson, W., Kleypas, J., Fabry, V. J., Millero, F. J. (2004). Impact of anthropogenic CO_2 on the $CaCO_3$ system in the oceans. Science, 305:362–365.

69 A. Mucci, *Am. J. Sci.* 238, 780 (1983).

70 F. J. Millero, *Geochim. Cosmochim. Acta* 59, 661 (1995).

71 The Royal Society (2005). Ocean Acidification due to increasing atmospheric carbon dioxide. Policy Document 12/05. http://royalsociety.org/document.asp?id=3249

II. GLOBAL STATUS AND TRENDS OF OCEAN ACIDIFICATION

The global atmospheric concentration of CO_2 has increased from a pre-industrial value of approximately 280 parts per million (ppm) to 384 ppm in 2007[72] (~387 ppm in 2009[73]), with half of this increase occurring within the last 30 years[74]. It is suggested that the current atmospheric CO_2 concentration is higher than has been experienced on Earth for 800,000 years[75]. However, in the absence of anthropogenic CO_2 uptake by the oceans, atmospheric CO_2 levels would be ~55 ppm higher than present, and the effects of global climate change more marked[76]. While the uptake of CO_2 by the oceans is buffering the extent of global climate change, ocean chemistry is changing at a rapid and unprecedented rate[77].

The surface waters of the oceans are slightly alkaline, with an overall mean pH of ~8.1 on the seawater scale[78]. During the past 250 years the average sea surface pH has decreased by about 0.1pH units, equivalent to a 30% increase in hydrogen ions—a considerable acidification of the oceans[79]. Atmospheric CO_2 concentrations are predicted to increase by 0.5–1.0% per year throughout the 21st century[80, 81]. Increasing ocean acidification follows directly (albeit with a time lag) the accelerating trend in world CO_2 emissions, and the magnitude of ocean acidification can be predicted with a high level of certainty based on the complex but predictable marine carbonate chemistry reactions and cycles described in the previous section. Along with the decline in surface water pH, a substantial change in carbonate chemistry (through changes in pCO_2, pH, A_T, and mineral saturation states) will occur, including a decline in carbonate ion concentration[82]. The impacts of ocean acidification on marine organisms and ecosystems are much less certain[83].

The closest geological analogue to the current atmospheric CO_2 concentrations is the Paleocene-Eocene thermal maximum (PETM), which occurred fifty-five million years ago. During this period a strong ocean acidification event occurred, marked by the rapid and massive carbon input to the ocean-atmosphere system. This event was characterised by a shoaling of the deep calcite saturation horizon by 2 km and a sharp sea surface temperature rise of 5–9°C over a limited time period of 1,000–2,000 years, leading to shifts in marine planktonic communities[84, 85]. The only major extinctions occurred within the

72 Solomon, S., Quinn, D., Manning, M., Chen, Z., Marquis, M., Averyt, K. B., Tignor, M., Miller, H. (eds) (2007). Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change. New York: Cambridge University Press.

73 Feely pers comm..

74 Inter-Academy Panel on International Issues (IAP). 2009. Statement on Ocean Acidification. Endorsed, June 2009. www.interacademies.net/CMS/9075.aspx

75 Luthi, D., Le Floch, M., Bereiter, M., Blunier, T., Barnola, J. M., *et al.* (2008). High-resolution carbon dioxide concentration record 650,000 – 800,000 years before present. Nature 453:379–382.

76 Solomon, S., Quinn, D., Manning, M., Chen, Z., Marquis, M., Averyt, K. B., Tignor, M., Miller, H. (eds) (2007). Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change. New York: Cambridge University Press.

77 Turley, C. M., Roberts, J. M., Guinotte, J. M. (2007). Corals in deepwater: will the unseen hand of ocean acidification destroy cold-water ecosystems. Coral Reefs 26:445–448.

78 Feely, R. A., Doney, S. C., and S.R. Cooley (2009), Ocean Acidification: Present conditions and future changes in a high-CO_2 world, Oceanography, submitted for publication.

79 The Royal Society (2005). Ocean Acidification due to increasing atmospheric carbon dioxide. Policy Document 12/05. http://royalsociety.org/document.asp?id=3249

80 Guinotte. J., Fabry, V. J. (2009) The Threat of Acidification to Ocean Ecosystems. The Journal of Marine Education, Vol, 25 (1):2–7.

81 Kleypas, J. A., Feely, R. A., Fabry, V. J., Langdon, C., Sabine, C. L., Robbins, L. L. (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 U.S Geological Survey, 88 pp.

82 The Royal Society (2005). Ocean Acidification due to increasing atmospheric carbon dioxide. Policy Document 12/05. http://royalsociety.org/document.asp?id=3249

83 Ibid.

84 Kennett, J. P., Stott, L. D. (1991). Abrupt deep-sea warming, paleoceanographic changes and benthic extinctions at the end of the Paleocene. Nature, 353:225–229.

85 Zachos, J. C., Rohl, U., Schellenberg, S. A., Slujis, A., Hodell, D. A., *et al.* (2003). Rapid acidification of the ocean during the Paleocene-Eocene thermal maximum. Science, 308:1611–1615.

benthic foraminifera, though it is unclear whether ocean acidification was the main factor or whether changes in ocean circulation led to anoxia in bottom waters[86]. A total of five mass extinction events have greatly influenced paths of evolution of life on Earth since the end of the Ordovician period (434 million years ago), significantly impacting coral reef ecosystems. The causes attributed to each mass extinction can be divided into those independent of the carbon cycle, such as direct physical destruction, disease and loss of biodiversity, and those linked to the carbon cycle, for example, acid rain. An examination by Veron indicates that the primary causes of each event can be linked in various ways to a perturbation of the carbon cycle in general, and changes in ocean chemistry in particular, with clear association to atmospheric CO_2 levels[87].

The fossil record for benthic calcified organisms, including reef-building corals and calcareous algae, shows a notable gap during the early Triassic period (250 million years ago) when atmospheric CO_2 concentrations increased dramatically to a level five times higher than present day[88], and recovery took hundreds of thousands of years[89]. By 2050 ocean pH is predicted to be lower than it has been for around 20 million years[90], and lessons from the Earth's past raise concerns that ocean acidification could trigger a sixth mass extinction event, independently of anthropogenic extinctions that are currently taking place[91].

Ocean acidification is a global issue. However, regional and seasonal influences, combined with the biological, chemical and physical factors (e.g. carbonate chemistry, biological productivity, and the effects of temperature on CO_2 solubility), influence the uptake of CO_2 and result in a variable mixed surface layer pH and magnitude of ocean acidification across the global oceans of ±0.3 units from about pH 7.90 to pH 8.20[92]. Larger variations can be observed from pH 7.3 inside deep estuaries to pH 8.6 in productive coastal plankton blooms, and pH 9.5 in tide pools. Because anthropogenic CO_2 invades the ocean by gas exchange across the air-sea interface, the highest concentrations of anthropogenic CO_2 are found in near surface waters[93].

A. SURFACE WATERS OF HIGH LATITUDE REGIONS

Colder waters, due to their higher solubility for CO_2, naturally hold more CO_2 and are more acidic than warmer waters[94]. It is suggested that with increasing atmospheric CO_2 concentrations, the surface waters of high latitude oceans will be the first to become under-saturated with respect to calcium carbonate[95]. Models of atmospheric CO_2, including ocean circulation, and geographical variations in temperature have indicated that the cold Southern Ocean is particularly vulnerable to changes in car-

86 Zachos, J. C., Dickens, G. R., Zeebe, R. E. (2008). An early Cenozoic perspective on greenhouse warming and carbon cycle dynamics. Nature, 451:279–83.

87 Veron, J. E. N. (2008) Mass extinctions and ocean acidification: biological constraints on geological dilemmas. Coral Reefs 27:459–472.

88 Hoegh-Guldberg, O., Mumby, P. J., Hooten, A. J., Steneck, R. S., Greenfield, P., Gomez, E., Harvell, C. D., Sale, P. F., Edwards, A. J., Caldeira, K., Knowlton, N., Eakin, C. M., Iglesias-Prieto, R., Muthiga, N., Bradbury, R. H., Dubi, A., and Hatziolos, M. E. (2007). Coral reefs under rapid climate change and ocean acidification. Science 318, 1737–1742.

89 MCCIP (2009). Marine Climate Change Ecosystem Linkages Report Card 2009. (Eds. Baxter, J. M., Buckley, P. J., Frost, M. T.), Summary Report, MCCIP, Lowestoft, 16pp.

90 Turley, C. M., Roberts, J. M., Guinotte, J. M. (2007). Corals in deepwater: will the unseen hand of ocean acidification destroy cold-water ecosystems. Coral Reefs 26:445–448.

91 Veron, J. E. N. (2008) Mass extinctions and ocean acidification: biological constraints on geological dilemmas. Coral Reefs 27:459–472.

92 The Royal Society (2005). Ocean Acidification due to increasing atmospheric carbon dioxide. Policy Document 12/05. http://royalsociety.org/document.asp?id=3249

93 Sabine, C. L., Freely, R. A., Gruber, N., Key, R. M., Lee, K., Bullister, J. L., *et al.* (2004). The oceanic sink for CO_2. Science, 305:367–371.

94 Guinotte, J. M., Fabry, V. J. (2008). Ocean acidification and its potential effects on marine ecosystems. Ann. N. Y. Acad. Sci. 1134: 320.

95 Cao, L., Caldeira, K. (2008). Atmospheric CO_2 Stabilization and Ocean Acidification. Geophys. Res. Lett. Vol 35:LI9609.

bonate saturation state due to the low existing saturation levels[96], uniform temperatures and the extent of mixing in the water column. Global models suggest that given current emission rates, the surface waters of the Southern Ocean will become under-saturated with respect to aragonite by the year 2050, and that by 2100 this under-saturation could extend throughout the entire Southern Ocean and into the subarctic North Pacific Ocean. At this point, the average surface ocean carbonate ion concentration will have decreased by nearly 50%[97]. Seasonal fluctuations in carbonate saturation imply that winter under-saturation for aragonite could occur earlier, projected in one model to occur by the year 2030 and no later than 2038 under the IPCC "business as usual" scenario[98]. These predictions suggest that detrimental conditions for the continuing function of marine ecosystems, especially calcifying organisms, could develop on much shorter timeframes than previously thought[99], and that natural variability in carbon dynamics will influence the onset of future ocean acidification.

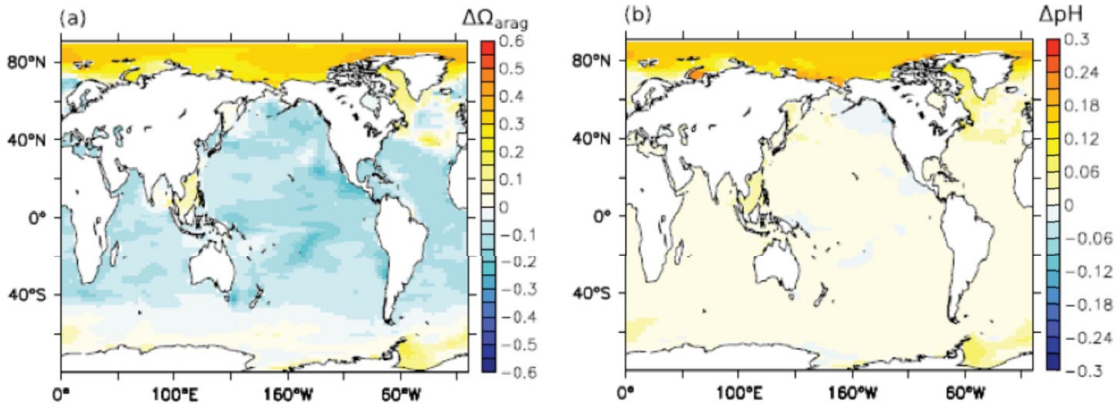


FIGURE 8. Difference in projected surface aragonite saturation (a) and pH (b) between the Special Report on Emissions Scenario A2 (medium-low emissions) simulation with and without warming, averaged over the decade 2090–2099. Positive values indicate enhanced acidification by climate change, negative values indicate reduced acidification. *Source: Steinacher,* et al. *(2009)*[100]

Recent predictions suggest that the largest pH changes in this century will occur in the surface waters of the Arctic Ocean, where hydrogen ion concentration could increase by up to 185% (a decrease in pH of 0.45 units) if the release of anthropogenic emissions continues along current trends[101]. In this instance, the Arctic mean annual Ω_{arag} <1 will be reached in 2032, reaching Ω_{arag} <0.75 before 2060 (Figure 8). This signifies that the waters will be corrosive to Arctic calcifers such as pteropods (shelled planktonic snails), and bivalves such as clams, which play a key role in Arctic marine food webs[102]. Furthermore,

96 OSPAR Commission (2006). Effects of the marine environment of ocean acidification resulting from elevated levels of CO_2 in the atmosphere.

97 Feely, R. A. Ocean Acidification Along the West Coast of North America. Part of Ocean Acidification: The Other Climate Change Story – Year of Science 2009 website www.yearofscience2009.org.

98 McNeil, B. I., and R. J. Matear (2008), Southern Ocean acidification: A tipping point at 450-ppm atmospheric CO_2, Proceedings of the National Academy of Sciences, _105(48), 18860–18864 doi:10.1073/pnas.0806318105

99 Orr, J. C., Fabry, V. J., Aumont, O., Bopp, L., Doney, S. C., *et al.* (2005). Anthropogenic ocean acidification over the twenty-first century and its impact on calcifying organisms. Nature 437:681–686.

100 Steinacher, M., Joos, F., Frölicher, T. L., Plattner, G.-K., Doney, S. C. (2009). Imminent ocean acidification in the Arctic project with the NCAR global coupled carbon cycle-climate model. Biogeosciences, 6:515–533.

101 Ibid.

102 Inter-Academy Panel on International Issues (IAP). 2009. Statement on Ocean Acidification. Endorsed, June 2009. www.interacademies.net/CMS/9075.aspx

the projected implications of climate change (freshening and sea ice retreat) during this period are likely to amplify the decrease in Arctic surface mean saturation and pH by more than 20%[103].

Time series observations in the Iceland Sea between 1985 and 2008 support modelled implications, demonstrating a winter decrease in surface water pH of 0.0024 yr^{-1}, which is 50% faster than observations from subtropical time series stations, and a faster rate of change than that observed in the deep water regime (>1,500m)[104]. The Iceland Sea is an important source of North Atlantic Deep Water and is host to ecologically significant cold water corals, which are highly sensitive to the ambient environment and have narrow growth parameters[105].

The shallowing or "shoaling" of the aragonite saturation horizon due to the rapid uptake of human-produced CO_2 is predicted to occur in all polar waters within this century[106]. The aragonite saturation horizon in the deep Arctic Ocean is currently at 2,500m, while the horizon depth in the Iceland Sea is 1,750m and rising at 4m yr^{-1} [107]. Due to the local elevation of the sea floor in the Iceland Sea a further 800km^2 of sea floor, previously bathed in saturated waters, is exposed to under-saturated conditions each year[108]. In the eastern South and North Atlantic, the aragonite saturation horizon has already migrated upwards by up to 150 metres in places. Accordingly, few records of cold-water framework-forming corals exist in the North Pacific where the aragonite saturation horizon is shallow (50–600 m), suggesting that the saturation state is limiting scleractinian (stony, reef-building) coral distribution and calcification rates[109].

B. SURFACE WATERS OF TEMPERATE REGIONS

Little published empirical information exists on the dynamics of directly measured ocean pH at temperate and mid-latitudes[110]. The Mediterranean Sea, for example, is warmer and more alkaline than the open ocean throughout the water column, resulting in a larger potential pH decrease relative to the Atlantic Ocean and the potential to remain saturated throughout most of the water column for many years to come[111]. However, a high resolution dataset of pH spanning eight years at a north-temperate coastal site at Tatoosh Island, USA reveals a general declining trend in pH over the observation period, alongside significant annual and diurnal fluctuations in pH, likely a result of photosynthesis, respiration and dynamic and seasonal mixing processes[112].

In regions of high biological productivity and export, DIC is converted into organic carbon by phytoplankton and exported by the biological pump into the deeper oceans[113]. Wind-driven, seasonal up-

103 Steinacher, M., Joos, F., Frölicher, T. L., Plattner, G.-K., Doney, S. C. (2009). Imminent ocean acidification in the Arctic project with the NCAR global coupled carbon cycle-climate model. Biogeosciences, 6:515–533.

104 Olafsson, J., Olafsdottir, S. R., Benoit-Cattin, A., Danielsen, M., Arnarson, T. S., Takahashi, T. (2009). Rate of Iceland Sea acidification from time series measurements. Biogeosciences Discuss, 6:5251–5270.

105 Freiwald, A., Fossa, J. H., Grehan, A., Koslow, T., Roberts, J. M. (2004). Cold-water Coral Reefs. UNEP-WCMC, Cambridge, UK.

106 Turley, C. M., Roberts, J. M., Guinotte, J. M. (2007). Corals in deepwater: will the unseen hand of ocean acidification destroy cold-water ecosystems. Coral Reefs 26:445–448.

107 Olafsson, J., Olafsdottir, S. R., Benoit-Cattin, A., Danielsen, M., Arnarson, T. S., Takahashi, T. (2009). Rate of Iceland Sea acidification from time series measurements. Biogeosciences Discuss, 6:5251–5270.

108 Ibid.

109 Feely, R. A., Sabine, C. L., Lee, K., Berelson, W., Kleypas, J., Fabry, V. J., Millero, F. J. (2004). Impact of anthropogenic CO_2 on the $CaCO_3$ system in the oceans. Science, 305:362–365.

110 CIESM, 2008. Impacts of acidification on biological, chemical and physical systems in the Mediterranean and Black Seas. N° 36 in *CIESM Workshop Monographs* [F. Briand Ed.], 124 pages, Monaco

111 Ibid.

112 Wootton, T. J., Pfister, C. A., Forester, D. (2008). Dynamic patterns and ecological impacts of declining ocean pH in a high-resolution multi-year dataset. PNAS, Vol. 105(48): 18848–18853.

113 The Royal Society (2005). Ocean Acidification due to increasing atmospheric carbon dioxide. Policy Document 12/05. http://royalsociety.org/document.asp?id=3249

welling of subsurface waters along temperate coastlines brings CO_2-enriched waters onto the shelf and, in some instances, into the surface ocean. This water contains a high level of CO_2 resulting from natural respiration processes in the subsurface layers and is also significantly contaminated with anthropogenic CO_2.

Along the west coast of North America for example, the seasonal upwelling of water under-saturated with respect to aragonite is observed on the continental shelf, reaching depths of 40–120 m (Figure 9)[114]. While this is a natural phenomenon in the region, the oceanic uptake of anthropogenic CO_2 has increased the areal extent and the potential threat of these acidified waters to many of the calcifying species that live along the coast[115].

The upwelling waters along this coast contain CO_2 levels at the edge of solubility for $CaCO_3$ aragonites (900 – 1,000 ppm), yet are estimated to have been last at the surface and in contact with the atmosphere, approximately 50 years ago when atmospheric CO_2 concentrations were ~310ppm, significantly lower than today (~384ppm)[116].

It has been tentatively proposed that ocean acidification will act to increase the oligotrophic nature of the Mediterranean Sea and increase the degree of phosphorous limitation currently found, which will contribute to reduced productivity and export[117]. As explained in subsequent sections, some of the world's most productive fisheries are associated with coastal zones in temperate latitudes, suggesting that the impacts on marine food webs caused by ocean acidification could be severe and a more urgent issue than previously thought. This regional scenario is indicative of the future ecological and social implications of upwelling corrosive waters that will likely be exacerbated throughout the next half century as water that has been exposed to increasing levels of atmospheric CO_2 is cycled through the system[118].

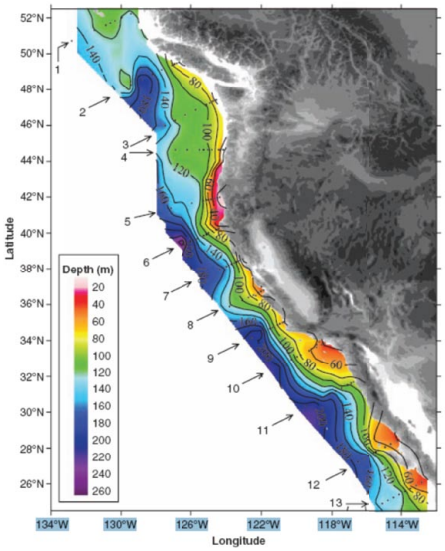


FIGURE 9: Depth distribution of under-saturated water on the continental shelf of western North America from Queen Charlotte Sound, Canada, to San Gregorio, Mexico. *Source: Feely* et al., *2008*[122].

114 Feely, R. A., Sabine, C. L., Hernandez-Ayon, J. M., Lanson, D., Hales, B. (2008). Evidence for Upwelling of Corrosive "Acidified" Water onto the Continental Shelf. Science, Vol320:1490 -1492.

115 Feely, R. A. *Ocean Acidification Along the West Coast of North America.* Part of *Ocean Acidification: The Other Climate Change Story.* www.yearofscience2009.org.

116 UNESCO, IGBP, MEL, SCOR. (2009). Ocean Acidification: A Summary for Policymakers from the Second Symposium on the Ocean in a High-CO_2 World. www.ocean-acidification.net

117 CIESM, 2008. Impacts of acidification on biological, chemical and physical systems in the Mediterranean and Black Seas. N° 36 in *CIESM Workshop Monographs* [F. Briand Ed.], 124 pages, Monaco

118 ScienceDaily (May 23 2008). U.S Pacific Coast Waters Turning More Acidic – www.sciencedaily.com/releases/2008/05/080522181511.htm

119 Feely, R. A., Sabine, C. L., Hernandez-Ayon, J. M., Lanson, D., Hales, B. (2008). Evidence for Upwelling of Corrosive "Acidified" Water onto the Continental Shelf. Science, Vol320:1490 -1492.

C. SURFACE WATERS OF TROPICAL REGIONS

Warming of the oceans leads to increased vertical stratification within the water column and reduced mixing between the layers, as is often observed in tropical regions. Warmer surface waters have a lower solubility of CO_2, and receive a lower nutrient supply from deeper layers, which in turn reduces primary production rates, and the rate of CO_2 uptake from the atmosphere[120]. In tropical regions adverse changes in carbonate ion availability as a result of decreasing pH are likely to be exacerbated by the lack of mixing between the warm, shallow, CO_2-enhanced surface layers and the buffering effects of cool, deep ocean waters[121]. However, in localised areas, such as the eastern tropical Pacific (ETP), surface waters have lower pH, lower carbonate saturation, and higher pCO_2 values relative to other tropical marine areas due to upwelling processes which mix CO_2 enriched, deep waters into the surface layers along a shallow thermocline[122].

Carbonate coral reefs do not exist in waters with carbonate-ion concentrations of less than 200 µmol kg^{-1}. Currently, carbonate ion concentrations are ~210µmol kg^{-1}, lower than at any time during the past 420,000 years[123]. According to recent model predictions, almost all tropical and sub-tropical reefs were surrounded by waters favourable to coral growth before the industrial revolution. The Great Barrier Reef, Coral Sea and the Caribbean Sea are predicted to experience low levels of aragonite saturation more rapidly than other tropical regions (e.g. Central Pacific) as atmospheric CO_2 concentrations increase[124].

D. NATURALLY LOW pH ENVIRONMENTS

There are several areas in the world's oceans which have a low pH or are already experiencing undersaturation with respect to $CaCO_3$ minerals, as is observed where volcanic processes cause CO_2 to vent from submarine sediments (Figure 10). In these areas, CO_2 reacts with the seawater, causing pH and chemistry changes. Such environments provide an ecosystem-scale validation of the predicted impacts of increasing pCO_2 and acidification on organisms and habitat structures, and can be examined to provide further information on the ecological tipping points at which principal groups of marine organisms are affected by increasing pCO_2[125].

In a coastal cold-vent area off the island of Ischia in Italy, nearly pure CO_2 bubbles from the seafloor in around 6 metres water depth. The mean pH directly around the vents is reduced by 0.6 – 1.5 units (pH 6.7 – 7.6), gradually rising to the normal pH value of 8.1 – 8.2 units at a distance of 70 – 120 metres from the vents. $CaCO_3$ (calcite and aragonite) saturation levels and pCO_2 concentrations display similar sliding ranges[126].

120 The Royal Society (2005). Ocean Acidification due to increasing atmospheric carbon dioxide. Policy Document 12/05. http://royalsociety.org/document.asp?id=3249

121 Veron, J. E. N. (2008) Mass extinctions and ocean acidification: biological constraints on geological dilemmas. Coral Reefs 27:459–472.

122 Manzello, D.P., Kleypas, J.A., Budd, D.A., Eakin, C.M., Glynn, P.W. and Langdon, C. (2008). Poorly cemented coral reefs of the eastern tropical Pacific: Possible insights into reef development in a high-CO_2 world. Proceedings of the National Academy of Sciences. Vol 105 (30). pp. 10450 - 10455

123 Hoegh-Guldberg, O., Mumby, P. J., Hooten, A. J., Steneck, R. S., Greenfield, P., Gomez, E., Harvell, C. D., Sale, P. F., Edwards, A. J., Caldeira, K., Knowlton, N., Eakin, C. M., Iglesias-Prieto, R., Muthiga, N., Bradbury, R. H., Dubi, A., and Hatziolos, M. E. (2007). Coral reefs under rapid climate change and ocean acidification. Science 318, 1737–1742.

124 Ibid.

125 Hall-Spencer, J. M., Rodolfo-Metalpa, R., Martin, S., Ransome, E., Fine, M., Turner, S. M., Rowley, S. J., Tedesco, D., Buia, M. C. (2008). Volcanic carbon dioxide vents show ecosystem effects of ocean acidification. Nature, Vol 454:96–99.

126 Ibid.

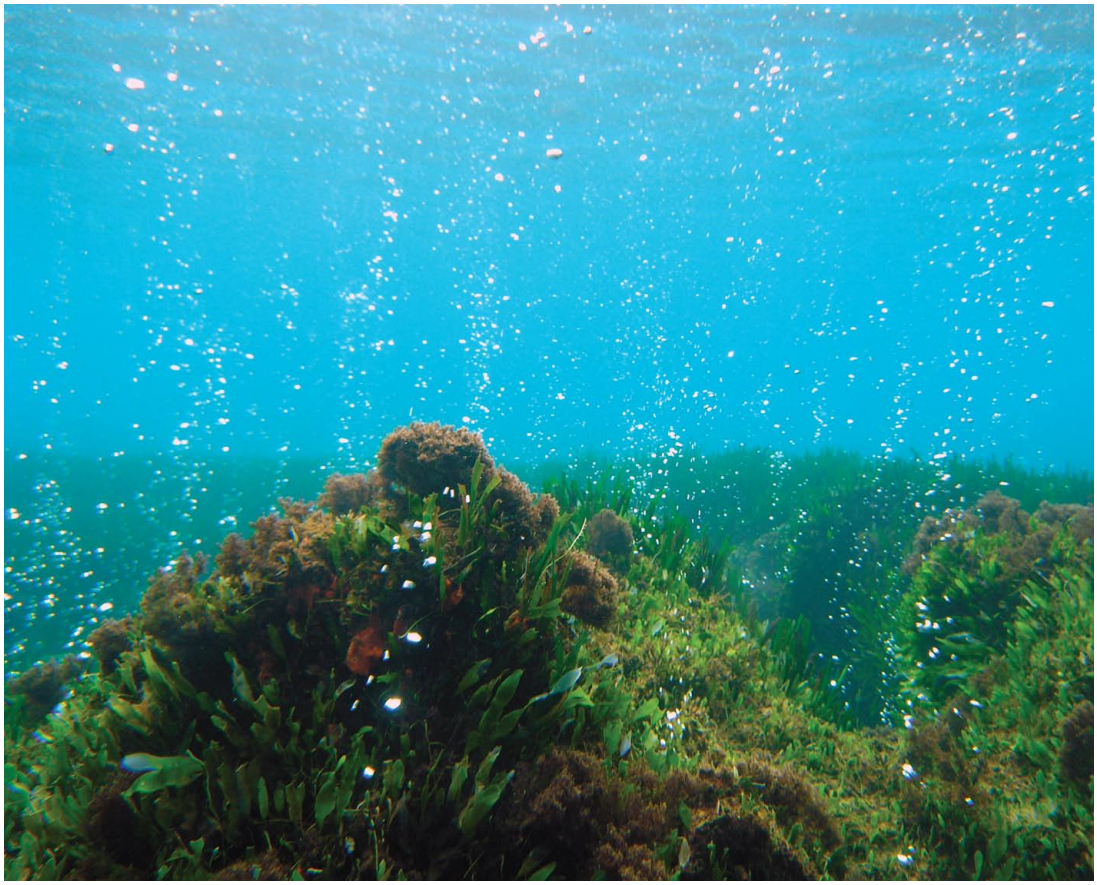


FIGURE 10: Bubbles from the CO_2 vent field at Ischia. *Source: Jason Hall-Spencer* et al. *2*008[127].

E. ANTHROPOGENIC ACTIVITIES

It is apparent that any increase in the amount of CO_2 in the oceans, due to natural- or human-induced fluxes, will exacerbate ocean acidification. This is of particular relevance for geo-engineering or macro-engineering activities that deliberately attempt to enhance CO_2 absorption and sequestration in the oceans, with a view to reducing atmospheric CO_2 concentrations and mitigating climate change. A portfolio of proposals for ocean storage of CO_2 has recently been reviewed by the IPCC to assess the feasibility and appropriateness of techniques[128]. Proposed mechanisms, including the direct injection of CO_2 into the water column ("dissolution type" injection) or onto the seafloor ("lake type" injection), while potentially able to temporarily remove CO_2 from the atmosphere, are more likely to exacerbate ocean acidification[129]. Ocean fertilization, i.e. any activity undertaken by humans with the principal intention of stimulating primary productivity in the oceans to induce biologically mediated CO_2 uptake from the atmosphere, also bears a high risk of changing ocean chemistry and pH, especially if carried

127 Hall-Spencer, J. M., Rodolfo-Metalpa, R., Martin, S., Ransome, E., Fine, M., Turner, S. M., Rowley, S. J., Tedesco, D., Buia, M. C. (2008). Volcanic carbon dioxide vents show ecosystem effects of ocean acidification. Nature, Vol 454:96–99.

128 IPCC (2005): IPCC Special Report on Carbon Dioxide Capture and Storage. Prepared by Working Group III of the Intergovernmental Panel on Climate Change [Metz, B., O. Davidson, H. C. de Coninck, M. Loos, and L. A. Meyer (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 442 pp

129 The Royal Society (2005). Ocean Acidification due to increasing atmospheric carbon dioxide. Policy Document 12/05. http://royalsociety.org/document.asp?id=3249

out repeatedly and at a large scale. The impacts (including ocean acidification effects) of ocean fertilization on marine biodiversity are synthesized in a separate report[130].

The addition of vast amounts of alkaline compounds, such as calcium hydroxide Ca $(OH)_2$ or magnesium hydroxide Mg $(OH)_2$, has been suggested as a mechanism to reduce atmospheric CO_2 while mitigating ocean acidification. However, uncertainties exist surrounding the efficiency of this method to effect significant changes in ocean acidification, and in regards to the localised effects and tipping points of alkalinity additions on saturation state and $CaCO_3$ precipitation[131]. Furthermore, the ecological damage to mine and transport alkaline minerals in sufficient quantities as would be required for such approaches to effect changes in ocean pH presents a major concern and is likely to make such approaches prohibitive[132].

F. FUTURE TRENDS

In 2000, the IPCC published a set of scenarios (Special Report on Emissions Scenarios – SRES), constructed to explore a range of global social, demographic, economic and technological developments, and the corresponding production of greenhouse gases. Estimates of future atmospheric and oceanic CO_2 concentrations, based on the scenario of the continued release of anthropogenic emissions along current trends ("business as usual" A2 & B1), and circulation models of the IPCC (IPCC IS92a) indicate that atmospheric CO_2 concentrations could exceed 500ppm by 2050, and 800ppm before 2100[133].

The corresponding decrease in surface water pH of between 0.14 and 0.3–0.4 units, to ~7.9, will be the equivalent of a 150% increase in hydrogen ion concentrations, and a 50% decrease in carbonate ion concentrations from pre-industrial levels[134]. The rate of change observed is at least 100 times more rapid than any experienced over the past 100,000 years[135]. This is significant for biological systems and gives little to no time for evolutionary adaptation to changes in ocean chemistry by marine organisms[136, 137].

Models of the "business as usual" scenario also indicate significant changes for global coastal ocean seawater chemistry and suggest a decline in the saturation state of the surface waters with respect to aragonite and calcite by 45% by the year 2100 and by 73% by the year 2300[138]. In addition, increases in atmospheric CO_2 and temperatures, and elevated levels of nutrients and organic matter in coastal areas are predicted to reduce $CaCO_3$ production rates by 40% by 2100 and will mean that $CaCO_3$ will be dissolving faster than it can be produced before 2150.

130 SCBD (in prep.) Scientific Synthesis on the Impacts of Ocean Fertilization on Marine Biodiversity. Technical Series No. 45, SCBD, Montreal.

131 www.cquestrate.com

132 The Royal Society (2005). Ocean Acidification due to increasing atmospheric carbon dioxide. Policy Document 12/05. http://royalsociety.org/document.asp?id=3249

133 Feely, R. A., Sabine, C. L., Hernandez-Ayon, J. M., Lanson, D., Hales, B. (2008). Evidence for Upwelling of Corrosive "Acidified" Water onto the Continental Shelf. Science, Vol320:1490 -1492.

134 Steinacher, M., Joos, F., Frölicher, T. L., Plattner, G.-K., Doney, S. C. (2009). Imminent ocean acidification in the Arctic project with the NCAR global coupled carbon cycle-climate model. Biogeosciences, 6:515–533.

135 OSPAR Commission (2006). Effects of the marine environment of ocean acidification resulting from elevated levels of CO_2 in the atmosphere.

136 Veron, J. E. N. (2008) Mass extinctions and ocean acidification: biological constraints on geological dilemmas. Coral Reefs 27:459–472.

137 Hoegh-Guldberg, O., Mumby, P. J., Hooten, A. J., Steneck, R. S., Greenfield, P., Gomez, E., Harvell, C. D., Sale, P. F., Edwards, A. J., Caldeira, K., Knowlton, N., Eakin, C. M., Iglesias-Prieto, R., Muthiga, N., Bradbury, R. H., Dubi, A., and Hatziolos, M. E. (2007). Coral reefs under rapid climate change and ocean acidification. Science 318, 1737–1742.

138 Andersson, A. J., Mackenzie, F. T., Lerman, A. (2006). Coastal Ocean CO_2 – carbonic acid- carbonate sediment system of the Anthropocene. Global Biogeochem. Cy., 20, doi:10.1029/2005GB002506.

One study to model the future of global coral reefs predicts that even at future atmospheric CO_2 concentrations of 450–500 ppm (a conservative estimate), carbonate-ion concentrations will drop below 200 µmol per kg^{-1}, beyond which $CaCO_3$-building reefs are no longer viable, and reef erosion will exceed calcification[139]. A change of this magnitude is believed to reduce coral reef ecosystems to less diverse and productive systems (Figure 11) [140].

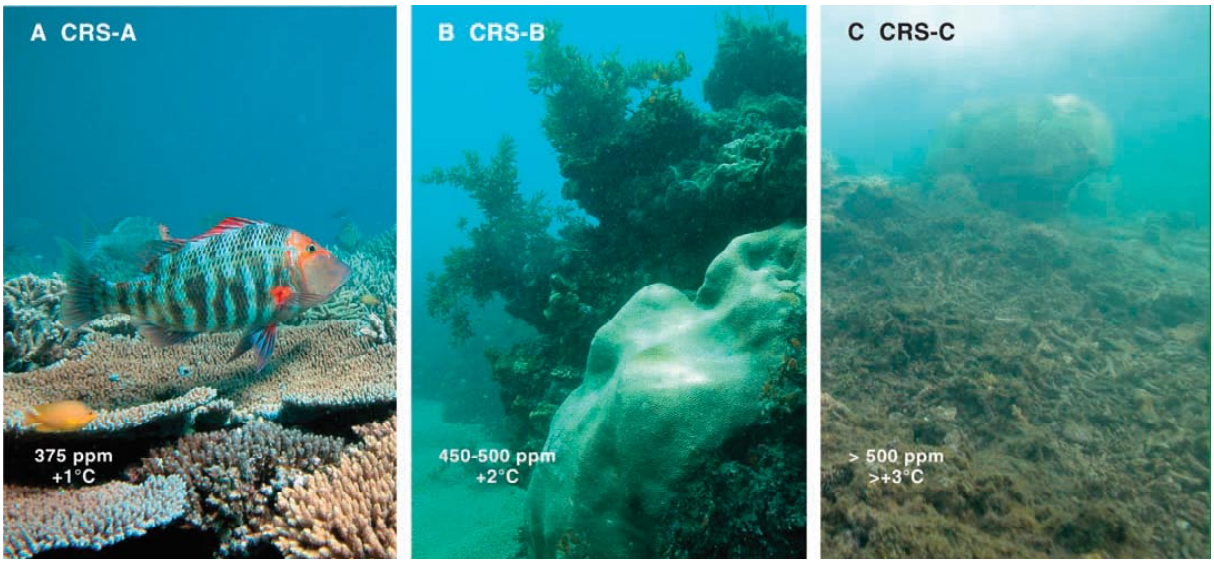


FIGURE 11: Analogs of the ecological structures predicted through three coral reef scenarios of increasing CO_2 and temperature, as shown. The $[CO_2]_{atm}$ and temperature increases shown are those for the scenarios and do not refer to the locations photographed. **A**. Reef slope community at Heron Island. **B**. Mixed algal and coral communities associated with inshore reefs around St. Bees Island near Mackay. **C**. Inshore reef slope around the Low Isles near Port Douglas. *Source: Hoegh-Guldberg* et al.*, 2007*[141].

Ocean acidification is irreversible on timeframes of at least tens of thousands of years[142] and is determined in the longer term by physical mixing processes within the ocean that allow ocean sediments to buffer the changes in ocean chemistry. Warming of the oceans as a result of global climate change may also reduce the rate of mixing with deeper waters, which would further delay recovery[143]. Despite the projected increase in dissolution rates and CO_2 uptake from the atmosphere, associated with decreasing $CaCO_3$ saturation states, it is likely that the rapid increases in atmospheric CO_2 concentrations could eventually overwhelm the natural buffering mechanisms of the ocean, leading to a reduced efficiency for carbon uptake by the oceans over the next two centuries[144]. Reduced buffering capacity of the ocean to take up CO_2 will increase the fraction of CO_2 retained in the atmosphere, a negative feedback loop leading to further ocean acidification.

139 Hoegh-Guldberg, O., Mumby, P. J., Hooten, A. J., Steneck, R. S., Greenfield, P., Gomez, E., Harvell, C. D., Sale, P. F., Edwards, A. J., Caldeira, K., Knowlton, N., Eakin, C. M., Iglesias-Prieto, R., Muthiga, N., Bradbury, R. H., Dubi, A., and Hatziolos, M. E. (2007). Coral reefs under rapid climate change and ocean acidification. Science 318, 1737–1742.

140 Ibid.

141 Hoegh-Guldberg, O., Mumby, P. J., Hooten, A. J., Steneck, R. S., Greenfield, P., Gomez, E., Harvell, C. D., Sale, P. F., Edwards, A. J., Caldeira, K., Knowlton, N., Eakin, C. M., Iglesias-Prieto, R., Muthiga, N., Bradbury, R. H., Dubi, A., and Hatziolos, M. E. (2007). Coral reefs under rapid climate change and ocean acidification. Science 318, 1737–1742.

142 Inter-Academy Panel on International Issues (IAP). 2009. Statement on Ocean Acidification. Endorsed, June 2009. www.interacademies.net/CMS/9075.aspx

143 The Royal Society (2005). Ocean Acidification due to increasing atmospheric carbon dioxide. Policy Document 12/05. http://royalsociety.org/document.asp?id=3249

144 Doney, S. C., Fabry, V. J., Feely, R. A., Kleypas, J. A. (2009). Ocean Acidification: The Other CO_2 problem. Annu. Rev. Mar. Sci. 1:169–192.

III. SYNTHESIS OF SCIENTIFIC INFORMATION ON POTENTIAL IMPACTS OF OCEAN ACIDIFICATION

A. METHODS AND APPROACHES TO ASSESS IMPACTS OF OCEAN ACIDIFICATION

Changing pH levels have potentially vast consequences for marine ecosystems because of the critical role pH plays in mediating physiological reactions. Furthermore, many important groups of marine organisms have a skeleton of $CaCO_3$, which dissolves when it reacts with corrosive acidified seawater. Hence, declining pH could interfere with critical processes, such as reef building, carbon sequestration via phytoplankton sedimentation, and consumer-resource interactions among marine organisms[145]. The ecosystem-wide response to changing pH is neither a simple function of having calcareous body parts, nor a general decline in organism function, and depends on the specific pH regulation and adaptation mechanisms of individual organisms, and the interplay among ecosystem components[146].

The current understanding of the response of marine organisms to ocean acidification has been based largely on in-vitro, short-term, tank and mesocosm experiments, leaving large knowledge gaps of the physiological and ecological impacts, and the broader implications for ocean ecosystems[147]. Despite recent advances, early studies have not included key variables, such as temperature, light and nutrients, known to affect calcification rates, and few observations are available over sufficient periods to indicate if organisms will be able to genetically adapt to the changes[148]. Furthermore, it is unknown if the observed responses of single species can be extrapolated to the genetically diverse populations that exist in natural ecosystems[149].

Experimental results have, however, clearly demonstrated that the rate of calcification in marine calcifiers is directly related to the seawater carbonate saturation state[150]. It can therefore be predicted that the goods and services provided by the ocean, upon which human populations are dependent, will be different under future acidified oceans as increasing partial pressure of CO_2, exerted by seawater (pCO_2) influences the physiology, development and survival of marine organisms[151]. The understanding of the short-term impacts of ocean acidification on different species of marine biota is building, and ongoing scientific experimentation is facilitating a growing understanding of the wider ecosystem and longer-term implications.

In the 1990s, several large-scale programmes (e.g. Joint Global Ocean Flux Study (JGOFS), Ocean Atmosphere Carbon Exchange Study (OACES)) were conducted to measure ocean carbonate chemistry and reconstruct historical CO_2 records. These programmes allowed the quantification of the past and current anthropogenic carbon in the oceans, regionally and with depth, and have been used to estimate changes in the calcite and aragonite saturation states. Observations from these programmes confirmed that over half of the anthropogenic carbon that has accumulated in the ocean is stored in the upper 400

145 Wootton, J. T., Pfister, C. A., Forester, J. S (2008). Dynamic patterns and ecological impacts of declining ocean pH in a high-resolution mutli-year dataset. Proc Natl Acad Sci U S A. 2008 December 2; 105(48): 18848–18853. Published online 2008 November 24. doi: 10.1073/pnas.0810079105

146 Ibid.

147 Hall-Spencer, J. M., Rodolfo-Metalpa, R., Martin, S., Ransome, E., Fine, M., Turner, S. M., Rowley, S. J., Tedesco, D., Buia, M. C. (2008). Volcanic carbon dioxide vents show ecosystem effects of ocean acidification. Nature, Vol 454:96–99.

148 ISRS (2008). Coral Reefs and Ocean Acidification. Briefing Paper 5, International Society for Reef Studies, 9pp.

149 The Royal Society (2005). Ocean Acidification due to increasing atmospheric carbon dioxide. Policy Document 12/05. http://royalsociety.org/document.asp?id=3249

150 Andersson, A. J., Mackenzie, F. T., Bates, N. R. (2008). Life of the margin: implications of ocean acidification on Mg-calcite, high latitude and cold-water marine calcifiers. Mar Ecol Prog Ser. Vol. 373:265–273.

151 Hofmann, G. E., O'Donnell, M. J., Todgham, A. E. (2008). Using functional genomics to explore the effects of ocean acidificiation on calcifying marine organisms. Mar Ecol Prog Ser, Vol. 373:219–225.

metres of the water column; these productive surface layers are also home to the majority of marine organisms[152].

A number of European projects have since been initiated (e.g. European Project on Ocean Acidification (EPOCA), BioAcid) to advance the understanding of the biological, ecological, biogeochemical and societal implications of ocean acidification, and to fill the existing knowledge gaps of physiological responses of marine organisms to acidifying oceans. A Guide to Best Practices in Ocean Acidification Research and Data Reporting has been prepared to provide guidance to the research community in this rapidly growing field[153].

Large-scale (60,000 litres) mesocosm experimental observation technology was tested for the first time in the Baltic Sea in 2009 to simulate future ocean pH conditions, under close-to-natural conditions (Figure 12). A comprehensive sampling programme using this technology, coordinated by the Leibniz Institute of Marine Sciences in Germany (IFM-GEOMAR), will be conducted in 2010 off Svalbard, Norway to gain further insights in vulnerable high latitudes. The study of sites with naturally elevated concentrations of CO_2 also provides opportunities to observe and advance the understanding of ocean acidification at the ecosystem level and on sufficient timeframes to observe the effects on communities of macro organisms[154].

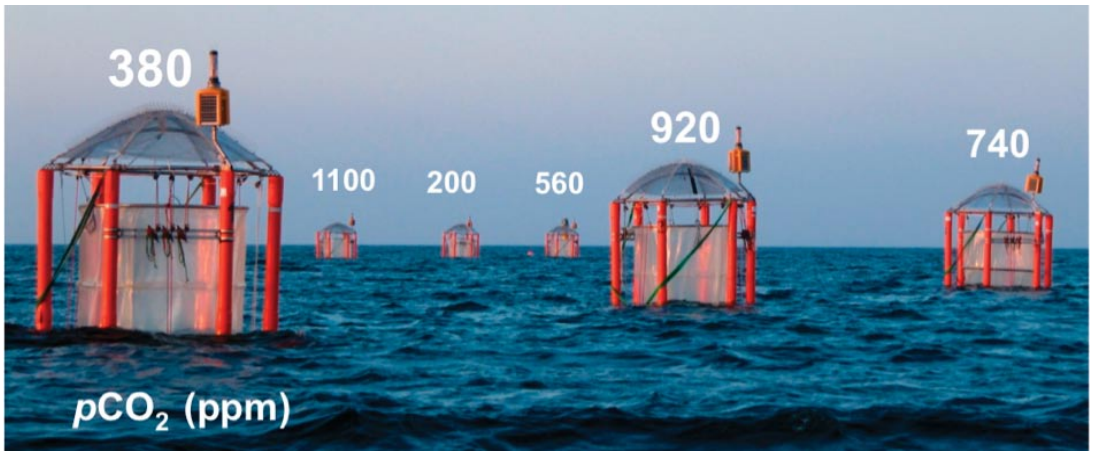


FIGURE 12. Large-scale experimental observation technology is tested in the Baltic Sea in 2009, under variable pCO_2 enrichment. *Source: Ulf Riebesell (IFM-GEOMAR).*

Evidence to date suggests that the impacts will be more varied than previously anticipated, with many species no longer viable, but some species able to adapt and proliferate. Ocean acidification will likely influence the biogeochemical dynamics of calcium carbonate, organic carbon, nitrogen, and phosphorus in the ocean as well as the seawater speciation of trace metals, trace elements and dissolved organic matter[155].

152 Kleypas, J. A., Feely, R. A., Fabry, V. J., Langdon, C., Sabine, C. L., Robbins, L. L. (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 U.S Geological Survey, 88 pp.

153 Riebesell, U., Fabry, V. J., Gattuso, J-. P. (2009). Guide to Best Practices in Ocean Acidification Research and Data Reporting. http://www.epoca-project.eu/index.php/Home/Guide-to-OA-Research/

154 Hall-Spencer, J. M., Rodolfo-Metalpa, R., Martin, S., Ransome, E., Fine, M., Turner, S. M., Rowley, S. J., Tedesco, D., Buia, M. C. (2008). Volcanic carbon dioxide vents show ecosystem effects of ocean acidification. Nature, Vol 454:96–99.

155 Doney, S. C., Fabry, V. J., Feely, R. A., Kleypas, J. A. (2009). Ocean Acidification: The Other CO_2 problem. Annu. Rev. Mar. Sci. 1:169–192.

B. THE ROLE OF $CaCO_3$ IN CALCIFYING ORGANISMS

Many marine organisms use carbonate minerals to form shells and skeletons , including crustose coralline algae, some phytoplankton, warm- and cold-water corals, and a range of pelagic and benthic invertebrates, from small pelagic swimming snails (pteropods) to lobsters. These organisms are important in almost all ecosystems, ranging from tropical regions to high latitudes and the deep sea[156]. The ability of these organisms to calcify is influenced by the acidity of the seawater, the availability of carbonate ions and temperature. Calcifying organisms are sensitive to changes in the saturation state of the important carbonate minerals calcite and aragonite. The overall saturation state of seawater is lower in high latitudes and deep waters than in low latitudes and shallower seas. Much less is known about how pH and saturation state vary in coastal ecosystems.

In general, magnesium (Mg) calcite minerals with a significant mole percent (mol %) $MgCO_3$ are more soluble than aragonite and calcite without Mg. The mole percent of magnesium deposited by marine organisms varies from a few mol % to as much as 30 mol % between different species[157], resulting in a significant response variation among taxa to changing ambient conditions[158]. Marine calcifiers depositing hard parts that contain significant concentrations of magnesium, high Mg-calcite, (e.g. Coralline red algae — the primary cementer that makes coral reef formation possible), alongside calcifying organisms living in high latitudes and cold-water environments, are at immediate risk from increasing ocean acidification, because they are already immersed in seawater that is only slightly supersaturated with respect to the carbonate phases they secrete[159].

The function of $CaCO_3$ is thought to change with lifecycle stage. Most experiments to date have focused on the lethal effects of CO_2 and acidification on adult organisms, and more information is needed on the sub-lethal impacts of small changes in pH to reproduction, growth rates and morphology in order to predict the longer-term ecosystem implications of ocean acidification[160]. The function of $CaCO_3$ in benthic and pelagic communities is discussed below, alongside the diverse responses of marine biota to increasing ocean acidification and increasing pCO_2, within the projected CO_2 emission scenarios.

C. BENTHIC COMMUNITIES

Benthic organisms have important functions within the marine ecosystem, enhancing sediment stability, providing habitat for small invertebrates and fish, and food for bottom dwelling and pelagic fisheries in shelf areas, and for humans. Continental shelves support a wealth of benthic calcifiers and calcifying communities, many of which are of direct economic importance or provide key support to fish habitats, and contribute to fundamental ecological processes. Table 2 summarizes the key benthic groups, the role of $CaCO_3$ in their functioning, and the observed impacts and implications of exposure to elevated CO_2 and decreasing pH.

156 Andersson, A. J., Mackenzie, F. T., Bates, N. R. (2008). Life of the margin: implications of ocean acidification on Mg-calcite, high latitude and cold-water marine calcifiers. Mar Ecol Prog Ser. Vol. 373:265–273.

157 Ibid.

158 Hofmann, G. E., O'Donnell, M. J., Todgham, A. E. (2008). Using functional genomics to explore the effects of ocean acidificiation on calcifying marine organisms. Mar Ecol Prog Ser, Vol. 373:219–225.

159 Andersson, A. J., Mackenzie, F. T., Bates, N. R. (2008). Life of the margin: implications of ocean acidification on Mg-calcite, high latitude and cold-water marine calcifiers. Mar Ecol Prog Ser. Vol. 373:265–273.

160 Kurihara, H., Shirayama, Y. (2004). Effects of increased atmospheric CO_2 on sea urchin early development. Mar Ecol Prog Ser. Vol 274:161–169.

TABLE 2: Summary of observed and predicted (*) impacts of high CO_2 and ocean acidification on benthic marine organisms.

Organism	Function of $CaCO_3$	Observed and predicted (*) impacts of elevated CO_2	Observed and predicted (*) impacts of low pH	Socio-ecological implications
Warm-water corals	Protection; anchoring to substrate; extension into water column; competition for space; stabilization of seafloor.	Potential to be outcompeted by non-calcifying species*[161]; Delay in reproduction due to slower growth rates[162]; Decrease in aragonite saturation state[163] Skeletal growth of most corals predicted to decrease by ~30% at atmospheric CO_2 concentrations of 560ppm*[164] 40% reduction in growth rates of crustose coralline algae observed under elevated CO_2 experimentation[165]. Net loss of $CaCO_3$ material from decreased calcification and increased dissolution in replicated sub-tropical reef community[166].	14.2 % decrease in coral calcification rates observed on the Great Barrier Reef[167] Decline in calcification rates linked to carbonate saturation state[168]; Two stony Mediterranean corals *Oculina patagonica* and *Madracis pharencis* maintained under low pH underwent complete skeleton dissolution but maintained health and recovered once returned to ambient conditions[169] New reef growth and accretion limited*[170];	Loss of ecosystem function e.g. storm and erosion defence[171]; Shift to higher export of organic matter, deposition and bacterial remineralization, creating zones of anoxia[172]; Synergistic effect of pervasive threats reducing reef health and viability[173];
Cold-water corals	Structural ecosystem framework	70% of known cold-water coral communities predicted to experience corrosive seawater by 2100, and by 2020 for some areas*[174];	Models predict a shoaling of the saturation horizon, reducing viable habitat[175]; 59% reduction in calcification rates observed in juvenile deep sea coral *Lophelia pertusa* compared with older polyps[176]	Dissolution of productive reef areas and loss of biodiversity and commercially important fish habitat; 40% of current fishing grounds are located in waters hosting cold-water corals[177]; may represent fish nursery habitats 85% of the economically important fish species observed on submersible transects in the waters off the Aleutian Islands were associated with cold-water corals[178].
Echinoderms	Protection; capture of prey; reproduction; buoyancy regulation; role in remineralization of sediment surfaces[179]. Metabolise highly soluble magnesium calcite.	*Hemicentrotus pulcherrimus* and *Echinodetra mathaei* showed reduction in reproduction success, developmental rates and larval size[180]. Reduction in fertilization rate once pH reached 7.1–7.0 units[181]. Exposure of brittlestar *Ophiothrix fragilis* to low pH resulted in a temporal decrease in larval size and abnormal development and skeletogenesis[182] Arm muscle wastage observed in burrowing brittlestar *A. filiformis* as a result of exposure to elevated CO[183].	Reduction in growth rates, size and body weight[184]; Test (shell) dissolution[185]; Abnormal morphology in pluteus larvae reducing competitive advantage. Brittlestar *Ophiothrix fragilis*, a keystone species of shelf seas in north-western Europe, showed 100% larval mortality as pH decreased by 0.2 units[186]. 25% reduction in sperm swimming speed, motility and reproductive success in sea urchin *Heliocidaris erythrogramma* under acidification of 0.4 pH units[187]. *H. erythrogramma* fertilization and early development observed to be robust to decreased pH within predicted values for environmental change[188].	Shift in marine ecosystem composition, loss of important functional group. Some echindoerms (urchins, sea cucumbers) constitute commercial fisheries.

Organism	Function of $CaCO_3$	Observed and predicted (*) impacts of elevated CO_2	Observed and predicted (*) impacts of low pH	Socio-ecological implications
Mollusc	Varied functions including structural and protective; passive defense; pH regulation; buoyancy control; oxidation of organic matter in pelagic sediments;[189]	Calcification rates of *Mytilus edulis* decreased by 25%[190] Particular sensitivity of juveniles; 70% of *Crassostrea gigas* larvae reared at pH 7.4 either completely non-shelled or partially shelled[191]. Calcification rates of oyster *Crassostrea gigas* decreased by 10%[192] Immune responses and organism health compromised in *Mytilus edulis* after 32 days exposure to elevated CO_2[193]; *Cephalopod Sepia officinalis* maintained calcification rates under elevated pCO_2 increasing body mass daily by ~ 4% and increasing the mass of the calcified cuttlebone by over 500%[194].	Reduced hatching of egg sacs in gastropod *Babylonia areolata*[195] 40% loss of sperm motility of *Crassostrea gigas following pH changes from pH8 to pH6*[196]. Juvenile clams *Mercenaria mercenaria* showed substantial shell dissolution and increased mortality[197]. Slower development time, altered embryonic movement and modification of shell shape in gastropod *Littorina obtusata* at lower pH[198] Reduced fertilization in Sydney rock oyster *Saccostrea glomerata* as a result of pCO_2 increases and temperature change from optimum[199]. 16% decrease in shell area and a 42% reduction in calcium content in oyster *Crassostrea virginica* grown in estuarine water under simulated pCO_2 regimes comparing preindustrial to 2100[200]. *Crassostrea ariakensis* larvae showed no change to either growth or calcification under the same treatments.	Loss of commercially and ecologically important marine species; Impact on livelihoods (aquaculture and fishing) and food security; Disruption of global food webs and predator-prey relationships[201];
Crustaceans		No observed effect of elevated CO_2 (2380ppm) on developmental rate, survival or body size in copepod *Acartia tsuensis*[202] Reduction in carapace mass and exoskeleton mineral content of carapace in the European lobster *Homarus gammaru* in CO_2-acidified sea water treatments[203]	No observed effect of reduced pH on barnacle *Amphibalanus Amphitrite* larval condition, cyprid (final larval stage) size, cyprid attachment and metamorphosis, juvenile to adult growth, or egg production[204].	

161 Atkinson, M. J., Cuet, P. (2008). Possible effects of ocean acidification on coral reef biogeochemistry: topics for research. Mar Ecol Prog Ser, Vol. 373:249–256.

162 Kleypas, J. A., Feely, R. A., Fabry, V. J., Langdon, C., Sabine, C. L., Robbins, L. L. (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 U.S Geological Survey, 88 pp.

163 Guinotte, J. M., Fabry, V. J. (2008). Ocean acidification and its potential effects on marine ecosystems. Ann. N. Y. Acad. Sci. 1134: 320.

164 Langdon, C., and M.J. Atkinson. 2005. Effect of elevated pCO_2 on photosynthesis and calcification of corals and interactions with seasonal change in temperature/irradiance and nutrient enrichment, Journal of Geophysical Research 110, CC09S07, doi:10.1029/2004JC002576.

165 Kuffner, I. B., *et al* (2007). Decreased abundance of crustose coralline algae due to ocean acidification. Nature Geoscience. 1:114–117.

166 Andersson, A. J., Kuffner, I. B., Mackenzie, F. T., Jokiel, P. L., Rodgers, K. S., & Tan, A., 2009. Net Loss of CaCO3 from a subtropical calcifying community due to seawater acidification: mesocosm-scale experimental evidence. Biogeosciences 6(8): 1811–1823

167 De'ath, G., Lough, J. M., Fabricius, K. E. (2009). Declining Coral Calcification on the Great Barrier Reef. Science Vol 323:116–119.

168 Leclercq, N., Gattuso, J. P. (2002). Primary production, respiration, and calcification of a coral reef mesocosm under increased CO_2 partial pressure. Limnol. Oceanogr. 47(2):558–564.

169 Fine, M., Tchernov, D. (2007). Scleractinian Coral Species Survive and Recover from Decalcification. Science, Vol 315:1811.

170 Hoegh-Guldberg, O., Mumby, P. J., Hooten, A. J., Steneck, R. S., Greenfield, P., Gomez, E., Harvell, C. D., Sale, P. F., Edwards, A. J., Caldeira, K., Knowlton, N., Eakin, C. M., Iglesias-Prieto, R., Muthiga, N., Bradbury, R. H., Dubi, A., and Hatziolos, M. E. (2007). Coral reefs under rapid climate change and ocean acidification. Science 318, 1737–1742.

171 Ibid.

172 Atkinson, M. J., Cuet, P. (2008). Possible effects of ocean acidification on coral reef biogeochemistry: topics for research. Mar Ecol Prog Ser, Vol. 373:249–256.

173 Gledhill, D. K., Wanninkhof, R., Millero, F. J., Eakin, M. (2008). Ocean Acidification of the Greater Caribbean Region 1996–2006. Journal of Geophysical Research Vol 113:C10031.

174 Guinotte, J. M., Orr, J., Cairns, S., Freiwald, A., Morgan, L., George, R. (2006). Will human-induced changes in seawater chemistry alter the distribution of deep-sea scleractinian corals? Front Ecol Environ 4(3):141–146.

175 Orr, J. C., Fabry, V. J., Aumont, O., Bopp, L., Doney, S. C., *et al.* (2005). Anthropogenic ocean acidification over the twenty-first century and its impact on calcifying organisms. Nature 437:681–686.

176 Maier, C., Hegeman, J., Weinbauer, M. G., Gattuso, J.-P. (2009). Calcification of the cold-water coral Lophelia pertusa under ambient and reduced pH. Biogeosciences, 6: 1671–1680.

177 WWF. 2004. Cold-water corals: fragile havens in the deep.

178 Stone, R. P., (2006). Coral habitat in the Aleutia Islands of Alaska: depth distribution, fine scale species associations and fisheries interactions. Coral Reefs, 25:229–238.

179 Gilbert, F. *et al.* 2007 Sediment reworking by marine benthic species from the Gullmar Fjord (Western Sweden) Importance of faunal biovolume. Journal of Experimental Marine Biology and Ecology 348: 133–144

180 Shirayama, Y., Thornton, H. (2005). Effect of increased atmospheric CO_2 on shallow water marine benthos. Journal of Geophysical Research, Vol, 110:C09S08

181 Kurihara, H., Shirayama, Y. (2004). Effects of increased atmospheric CO_2 on sea urchin early development. Mar Ecol Prog Ser, Vol. 274:161–169.

182 Dupont S., Havenhand J., Thorndyke W., Peck L. & Thorndyke M., 2008. Near-future level of CO_2-driven ocean acidification radically affects larval survival and development in the brittlestar Ophiothrix fragilis. Marine Ecology Progress Series 373:285–294.

183 Wood, H. L., Spicer, J. I., Widdicombe, S. (2008). Ocean acidification may increase calcification – but at a cost. Proc. R. Soc. Lond. B – Biol. Sci., 275(1644):1767–1773.

184 Michaelidis, B., Ouzounis, C., Paleras, A., Portner, H. O. (2005). Effects of long-term moderate hypercapnia on acid-base balance and growth rate in marine mussels Mytilus galloprovincialis. Mar Ecol Prog Ser 293:109–118.

185 Shirayama, Y., Thornton, H. (2005). Effect of increased atmospheric CO_2 on shallow water marine benthos. Journal of Geophysical Research, Vol, 110:C09S08

186 Dupont, S., Havenhand, J., Thorndykw, Q., Peck, L., Thorndyke, M. (2008). Near-future level of CO_2-driven ocean acidification rapidly affects larval survival and development in the britlestar Ophiothrix fragilis. Mar Ecol Prog Ser, Vol. 373:285–294.

187 Havenhand, J. N., Buttler, F. R., Thorndyke, M. C., Williamson, J. E. (2008). Near-future levels of ocean acidification reduce fertilization success in a sea urchin. Current Biology. Vol, 18(5):651–652.

188 Byrne, M., Ho, M., Selvakumaraswamy, P., Nguyen, H. D., Dworjanyn, S. A., Davis, A. R. (2009). Temperature, but not pH, compromises sea urchin fertilization and early development under near future climate change scenarios. Proc. R. Soc. B. 276:1883–1888.

189 Ingalls, A.E. *et al.* 2004 Organic matter diagenesis in shallow water carbonate sediments Geochimica et Cosmochimica Acta, 68 (21): 4363–4379

190 Gazeau, F., Quiblier, C., Jansen, J., Gattuso, J. P., Middleburg, J., Heip, C. (2007). Impact of elevated CO_2 on shellfish calcification. Geophys Res Lett 34:L07603.

191 Kurihara, H. (2008). Effects of CO2 driven ocean acidification on the early developmental stages of invertebrates. Mar Ecol Prog Ser, Vol. 373:275–284.

192 Gazeau, F., Quiblier, C., Jansen, J., Gattuso, J. P., Middleburg, J., Heip, C. (2007). Impact of elevated CO_2 on shellfish calcification. Geophys Res Lett 34:L07603.

193 Bibby, R., Widdicombe, S., Parry, H., Spicer, J., Pipe, R. (2008). Effects of ocean acidification on the immune response of the blue mussel Mytilus edulis. Aquatic Biology. Vol, 2:67–74.

194 Gutowska, M., Portner, H. O., Melzner, F. (2008). Growth and calcification in the cephalopod Sepia officinalis under elevated seawater pCO2. Mar Ecol Prog Ser 373:303–309.

195 Luo, J., Du, T., Liu, C. (2004). The influence of pH and salinity in hatching rate of egg sac of Babylonia areloate and the effect of different diet on the development, survival rate of the larvae. Marine Sciences/ Haiyang Kexue 28(6):5–9.

196 The Royal Society (2005). Ocean Acidification due to increasing atmospheric carbon dioxide. Policy Document 12/05. http://royalsociety.org/document.asp?id=3249

197 Green, M. A., Jones, M. E., Boudreau, C. L., Moore, R. L., Westman, B. A. (2004). Dissolution mortality of juvenile bivalves in coastal marine deposits. Limnology and Oceanography, 49:727–734.

198 Ellis, R. P., Bersey, J., Rundle, S., Hall-Spencer, J. M., Spicer, J. I. (2009). Subtle but significant effects of CO_2 acidified seawater on embryos of the intertidal snail, Littorina obtusata. Aquat Biol, Vol 5:41–018.

199 Parker, L. M., P. M. Ross, and W. A. O'Connor (2009), The effect of ocean acidification and temperature on the fertilization and embryonic development of the Sydney rock oyster Saccostrea glomerata (Gould 1850), Global Change Biology, 15(9), 2123–2136, doi:10.1111/j.1365–2486.2009.01895.x.

200 Miller, A. W., Reynolds, A. C., Sobrino, C., Reidel, G. F. (2009). Shellfish Face Uncertain Future in High CO_2 World: Influence of Acidification on Oyster Larvae Calcification and Growth in Estuaries. PLOSOne, Vol 4(5) e5561.

201 Cooley, S. R., Doney, S. C. (200). Economic vulnerability assessment of U.S. fishery revenues to ocean acidification. Submitted to Proceedings of the National Academy of Sciences of the United States of America. www.pnas.org/cgi/doi/10.1073/pnas.0709640104.

202 Kurihara, H., Ishimatsu, A. (2008). Effects of high CO_2 seawater on the copepod (Acartia tsuensis) through all life stages and subsequent generations. Mar Pollut Bull 56:1086–1090.

203 Arnold, K. E., Findlay, H. S., Spicer, J. I., Daniels, C. L., & Boothroyd, D., 2009. Effect of CO_2-related acidification on aspects of the larval development of the European lobster, Homarus gammarus (L.). Biogeosciences 6(8): 1747–1754.

204 McDonald, M. R., McClintock, J. B., Amsler, C. D., Rittschof, D., Angus, R. A., Orihuela, B., Lutostanski, K. (2008). Effects of ocean acidification over the life history of the barnacle Amphibalanus Amphitrite. Mar Ecol Prog Ser, Vol 385:179–187.

Warm-water Coral Reefs

Tropical coral reefs cover an area of 284,803km^2 and are limited in distribution by narrow growth parameters, occurring primarily in sunlit surface waters of the tropical and sub tropical oceans[205]. These diverse and productive ecosystems provide habitat for thousands of species and are important and valuable resources for people and industries, estimated to provide in excess of $30 billion annually in global goods and services, such as coastline protection, tourism, and protein. In Hawaii alone, reef-related tourism and fishing generate $360 million per year[206].

In corals and coralline algae, the development of $CaCO_3$ skeletal material provides rigidity against hydrodynamic conditions; facilitates anchorage to hard bottom substrates; plays a role in protection; and is thought to elevate the organism above the substrate into more optimal light and flow conditions, aiding growth and reproduction. The rate of coral calcification is an important barometer of the health of reef ecosystems.

Aragonite is the principal mineral deposit in the skeletal materials of reef-building Scleractinian corals. Aragonite is more soluble and has a significantly shallower saturation depth than calcite, making corals vulnerable to changes in saturation states[207]. As a result of increasing CO_2 concentrations, the aragonite saturation state has already decreased from preindustrial levels by ~16%[208]. A number of independent experiments have shown warm-water zooxanthellate corals to be sensitive to lower aragonite saturations with a corresponding reduction in their ability to calcify in high CO_2 waters[209]. Future projections of global aragonite saturation state indicate that while warm-water corals will experience lower saturation levels and may suffer from reduced calcification, it is the cold-water corals that are first likely to experience under-saturated conditions with respect to aragonite[210].

Experimental evidence has demonstrated that an increase in pCO_2 has a negative effect on coral and reef community calcification as a result of a decrease in the aragonite saturation state[211]. Investigations into the annual calcification rates of massive *Porities* spp. on the Great Barrier Reef (GBR) in Australia demonstrated a decline in calcification rates of 14.2% during the period 1990 – 2005 in the corals studied. The study was based on measurements of 328 colonies of massive *Porites* spp from 69 reefs ranging from coastal to oceanic locations and covering most of the (>2000km) length of the Great Barrier Reef. Sea surface temperature and carbonate saturation state are considered as the two most likely drivers affecting calcification on the GBR-wide scale[212]. Previous studies suggest that calcification rates could be reduced between 20–60% at double preindustrial atmospheric concentrations (560ppm)[213]; a reduction of this magnitude could fundamentally alter the reef structure and function of these important ecosystems, with deleterious consequences.

205 Spalding *et al* (2001) World Atlas of Coral Reefs.

206 TNC (2008). The Honolulu Declaration on Ocean Acidification and Reef Management: Workshop Report 12–14 August 2008.

207 Turley, C. M., Roberts, J. M., Guinotte, J. M. (2007). Corals in deepwater: will the unseen hand of ocean acidification destroy cold-water ecosystems. Coral Reefs 26:445–448.

208 Guinotte, J. M., Fabry, V. J. (2008). Ocean acidification and its potential effects on marine ecosystems. Ann. N. Y. Acad. Sci. 1134: 320.

209 Kleypas, J. A., Feely, R. A., Fabry, V. J., Langdon, C., Sabine, C. L., Robbins, L. L. (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 U.S Geological Survey, 88 pp.

210 Guinotte, J. M., Orr, J., Cairns, S., Freiwald, A., Morgan, L., George, R. (2006). Will human induced changes in seawater chemistry alter the distribution of deep-sea scleractinian corals? Front Ecol Environ 4:141–146

211 Leclercq, N., Gattuso, J. P. (2002). Primary production, respiration, and calcification of a coral reef mesocosm under increased CO_2 partial pressure. Limnol. Oceanogr. 47(2):558–564.

212 De'ath, G., Lough, J. M., Fabricius, K. E. (2009). Declining Coral Calcification on the Great Barrier Reef. Science Vol323:116–119.

213 Kleypas, J. A., Feely, R. A., Fabry, V. J., Langdon, C., Sabine, C. L., Robbins, L. L. (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 U.S Geological Survey, 88 pp.

The monitoring of direct calcification responses of corals to ocean acidification *in-situ* is complicated by the synergistic effect of factors other than basic seawater chemistry, including light, temperature and nutrients. Additionally, diurnal variability in carbonate chemistry is observed in waters over coral reefs following photosynthesis-respiration, and calcification-dissolution by the coral community.

Scleractinian corals *Oculina patagonica* and *Madracis pharencis,* maintained in an indoor flow-through system under ambient temperatures but reduced pH values of 7.3–7.6 and 8.0–8.3 for a period of 12 months, demonstrated complete skeleton dissolution but maintained basic functions without the loss of algal symbionts, substrate attachment, or reproductive capabilities. Once transferred to ambient pH conditions, the soft-bodied polyps calcified and reformed colonies, suggesting that corals may be capable of surviving large-scale environmental change[214]. However, this situation may not predominate in the natural environment given additional energy demands on the organism, such as predation pressure and variable food availability.

A net loss of $CaCO_3$ material was observed as a result of decreased calcification and increased carbonate dissolution from subtropical coral reef communities incubated in continuous-flow mesocosms subject to future seawater conditions. The calcifying community was dominated by the coral *Montipora capitata*. Daily average community calcification was positive at 3.3 mmol $CaCO_3$ m^{-2} h^{-1} under ambient seawater pCO_2 conditions as opposed to negative at −0.04 mmol $CaCO_3$ m^{-2} h^{-1} under seawater conditions of double the ambient pCO_2. These experimental results support the conclusion that some net calcifying communities could become subject to net dissolution in response to anthropogenic ocean acidification within this century. Nevertheless, individual corals remained healthy, actively calcified (albeit slower than at present rates), and deposited significant amounts of $CaCO_3$ under the prevailing experimental seawater conditions of elevated pCO_2[215].

Crustose coralline algae, an ubiquitous red algae, is of key importance in coral reef ecosystems, stabilizing reef structures and providing an important food source for benthic organisms such as sea urchins, parrot fish, and several species of mollusc[216], including commercially and culturally important abalone. Crustose coralline algae form a major calcifying component of the marine benthos from polar to tropical regions and are considered to influence the settlement of coral recruits. Laboratory experiments exposing algae to elevated CO_2 of up to two times present-day values indicated up to a 40% reduction in growth rates, a 78% decrease in the recruitment, and a 92% reduction in areal coverage[217]. In tropical and subtropical environments, the dependence of calcareous algae, and other important reef calcifiers, like echinoderms and benthic foraminifera, on high-magnesium calcite, the most soluble of all calcium carbonate minerals, would make these likely early casualties of ocean acidification. These algae are critical to reef consolidation; their demise would seriously threaten net accretion of reefs even before reduced calcification was a significant issue for scleractinian corals[218, 219].

As the world's oceans become less saturated with respect to carbonate minerals over time, corals are expected to build weaker skeletons and experience slower growth rates, which will make it more difficult

214 Fine, M., Tchernov, D. (2007). Scleractinian Coral Species Survive and Recover from Decalcification. Science, Vol 315:1811.

215 Andersson, A. J., Kuffner, I. B., Mackenzie, F. T., Jokiel, P. L., Rodgers, K. S., & Tan, A., 2009. Net Loss of CaCO3 from a subtropical calcifying community due to seawater acidification: mesocosm-scale experimental evidence. *Biogeosciences* 6(8): 1811–1823

216 Chisholm, J. R. M. (2000). Calcification by crustose corraline algae on the northern Great Barrier Reef, Australia. Limnol. Oceanogr. 45:1476–1484.

217 Kuffner, I. B., *et al* (2007). Decreased abundance of crustose coralline algae due to ocean acidification. Nature Geoscience. 1:114–117.

218 Veron, J. E. N. (2008) Mass extinctions and ocean acidification: biological constraints on geological dilemmas. Coral Reefs 27:459–472.

219 Kuffner, I. B., *et al* (2007). Decreased abundance of crustose coralline algae due to ocean acidification. Nature Geoscience. 1:114–117.

for corals to retain competitive advantage over other marine organisms[220, 221]. Increasingly brittle coral skeletons are at greater risk of storm damage, and bioerosion, which will reduce the structural complexity of the reef system, reducing habitat quality and diversity alongside the loss of coastal protection functions[222]. Coral reefs are threatened globally by a suite of anthropogenic and natural threats including human population growth, coral bleaching resulting from high temperature events, overfishing, coastal development, land-based pollution, nutrient run off and coral disease. An estimated 19% of the original global area of coral reefs has been effectively lost, with a further 35% threatened with loss within the next half century[223]. The climatic effects of rising ocean temperatures and ocean acidification further exacerbate the pervasive threats to reef ecosystems[224].

The response of tropical coral reefs to ocean acidification will range from the point where reduced skeletal growth affects the coral's ability to survive to the point where a reef loses the ability to maintain its structure. These "thresholds" will vary from coral to coral and from reef to reef. For example, the reproductive success and sexual maturity of some coral species such as *Goniastrea aspera* is dependent on size of the colony rather than age, and thus is likely to be reduced in low pH conditions where growth rates are slower[225]. It is suggested that skeletal growth of most corals will decrease by about 30% once atmospheric CO_2 concentration reaches 560ppm[226] and that many reefs will shift from a reef growth to erosion state, particularly in areas where other pervasive threats are prevalent[227].

The analysis of multiple coral reef sites on the eastern seaboard of Panama (Gulf of Panama and Gulf of Chiriqui) and the Galapagos Islands indicates that site specific water chemistry has a profound effect on coral reef growth and development. When compared to reefs in the Gulf of Mexico, the eastern tropical Pacific (ETP) reef frameworks are very poorly cemented and only held in place by a thin envelope of encrusting organisms. This makes them highly susceptible to bioerosion — indeed, the bioerosion rates of the ETP reefs studied are among the highest measured for any reef system to date. The study suggests that ETP reefs represent a real-world example of coral reef growth in low saturated waters that can provide an insight into how the biological-geological interface of coral reefs will change in a high-CO_2 world[228].

Cold-water Coral Communities

Cold-water coral communities or bioherms are found throughout the world's oceans between 200 and 1000 metres depth, in temperatures between 4°-12°C. Extensive carbonate reef frameworks covering

220 Guinotte, J. M., Orr, J., Cairns, S., Freiwald, A., Morgan, L., George, R. (2006). Will human-induced changes in seawater chemistry alter the distribution of deep-sea scleractinian corals? Front Ecol Environ 4(3):141–146.

221 Atkinson, M. J., Cuet, P. (2008). Possible effects of ocean acidification on coral reef biogeochemistry: topics for research. Mar Ecol Prog Ser, Vol. 373:249–256.

222 Hoegh-Guldberg, O., Mumby, P. J., Hooten, A. J., Steneck, R. S., Greenfield, P., Gomez, E., Harvell, C. D., Sale, P. F., Edwards, A. J., Caldeira, K., Knowlton, N., Eakin, C. M., Iglesias-Prieto, R., Muthiga, N., Bradbury, R. H., Dubi, A., and Hatziolos, M. E. (2007). Coral reefs under rapid climate change and ocean acidification. Science 318, 1737–1742.

223 Wilkinson, C. (2008). Status of Coral Reefs of the World: 2008. Global Coral Reef Monitoring Network and Reef and Rainforest Research Centre, Townsville, Australia, 296 p.

224 Gledhill, D. K., Wanninkhof, R., Millero, F. J., Eakin, M. (2008). Ocean Acidification of the Greater Carbibbean Region 1996–2006. Journal of Geophysical Research Vol 113:C10031.

225 Kleypas, J. A., Feely, R. A., Fabry, V. J., Langdon, C., Sabine, C. L., Robbins, L. L. (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 U.S Geological Survey, 88 pp.

226 Langdon, C., and M.J. Atkinson. 2005. Effect of elevated pCO_2 on photosynthesis and calcification of corals and interactions with seasonal change in temperature/irradiance and nutrient enrichment, Journal of Geophysical Research 110, CC09S07, doi:10.1029/2004JC002576.

227 TNC (2008). The Honolulu Declaration on Ocean Acidification and Reef Management: Workshop Report 12–14 August 2008.

228 Manzello, D. P., Kleypas, J. A., Budd, D. A., Eakin, M., Glynn, P. W., Langdon, C. (2008). Poorly cemented coral reefs of the eastern tropical Pacific: Possible insights into reef development in a high-CO_2 world Proc Natl Acad Sci U S A. 2008 July 29; 105(30): 10450–10455.

areas of over 100 km^2 (e.g. Røst Reef, Norway) built by six of the 700+ known species, play an important role as a refuge and feeding ground for organisms and commercial fish species[229], supporting characteristic fauna several times as diverse as that found on the surrounding seabed[230]. An estimated 40% of current fishing grounds are located in waters hosting cold-water coral communities[231]. These slow-growing, long-lived corals are especially vulnerable to stresses from anthropogenic activities such as bottom trawling, oil and gas exploration, and sub-marine industry activities (e.g. sub-marine cables), which act in tandem with pervasive stress from changes in ocean circulation and chemistry.

The carbonate saturation state generally decreases with latitude and depth, and thus the conditions inhabited by cold-water corals are often less favourable for calcification, being bathed in waters with naturally high levels of CO_2[232]. However, more than 95% of cold-water coral communities occur in waters that are supersaturated with respect to aragonite, confining their global distribution to ocean basins where the aragonite saturation horizon remains relatively deep (Figure 13). The predicted shoaling of the aragonite saturation horizon over time as atmospheric CO_2 concentrations increase may make large areas of the oceans uninhabitable for cold-water corals much earlier than for their warm water counterparts[233]. Indeed, according to predictions, 70% of known cold-water coral ecosystems could experience corrosive water conditions by the end of the century, although some may experience aragonite undersaturation as early as 2020[234, 235].

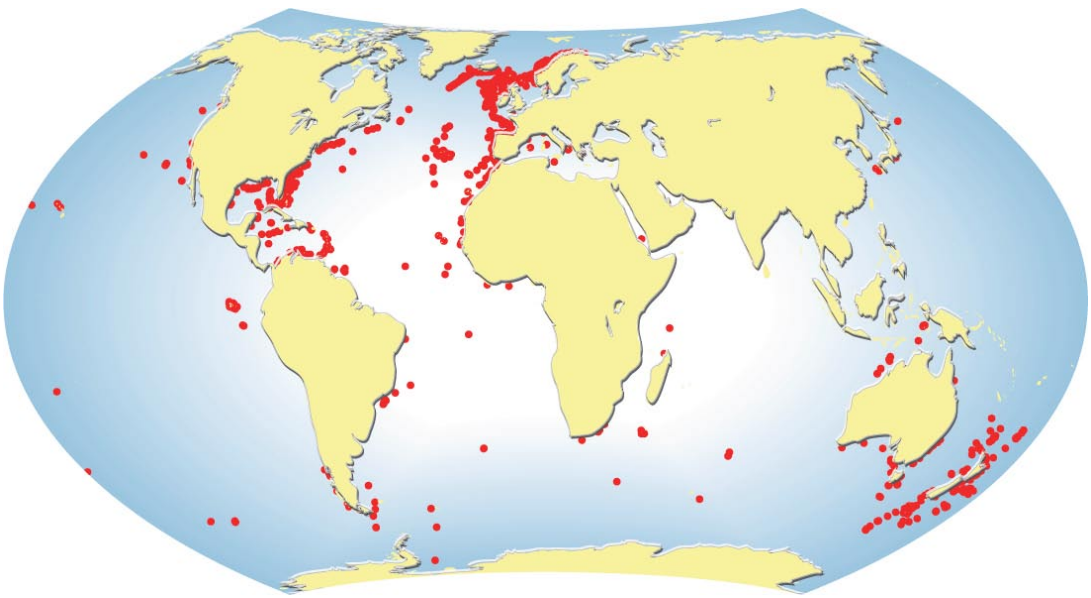


FIGURE 13: Global distribution of cold-water coral communities. *Source: Hugo Ahlenius, UNEP – WCMC 2005*[236]

229 Turley, C. M., Roberts, J. M., Guinotte, J. M. (2007). Corals in deepwater: will the unseen hand of ocean acidification destroy cold-water ecosystems. Coral Reefs 26:445–448.

230 Ibid.

231 WWF. 2004. Cold-water corals: fragile havens in the deep.

232 Guinotte. J., Fabry, V. J. (2009) The Threat of Acidification to Ocean Ecosystems. The Journal of Marine Education, Vol, 25 (1):2–7.

233 Guinotte, J. M., Orr, J., Cairns, S., Freiwald, A., Morgan, L., George, R. (2006). Will human-induced changes in seawater chemistry alter the distribution of deep-sea scleractinian corals? Front Ecol Environ 4(3):141–146.

234 Ibid.

235 Ibid.

236 http://maps.grida.no/go/graphic/coldwater-coral-reefs-distribution

Deep-water corals have evolved in cold, dark and nutrient-rich environments and rely on the flux of particulate organic matter from surface waters. Rising temperature and salinity changes caused by increasing CO_2 concentrations in the global oceans could alter circulation patterns and thus food availability for corals, and physiology and biochemistry, with significant consequences for these important ecosystems[237].

Cold-water coral communities have only recently been the focus of study following the development of sufficiently sophisticated instrumentation to explore deep-water environments. The first measurements of calcification rates in deep-sea coral conducted recently with *Lophelia pertusa* showed clear patterns of calcification, with the youngest polyps calcifying most rapidly, at rates comparable to those of slow-growing reef-building corals. Dramatically reduced calcification rates were observed at lower pH treatments as a clear response to increased pCO_2 and lower pH with juveniles suffering more (59% reduction) than older polyps (40% reduction)[238]. If the current rate of increase in CO_2 emissions continues unabated, ocean acidification could threaten sensitive cold-water coral environments before their biological diversity and importance has been effectively explored[239].

Echinoderms, Crustaceans, Molluscs

The role of $CaCO_3$ in echinoderms, crustaceans, molluscs and foraminifera varies depending on lifecycle stage, but $CaCO_3$ is essential to their existence and effective function. Physiological functions other than structural and protective ones include passive defense through pigmentation of the shell, and pH regulation through sealing off the supply of ambient sea water, as seen in the barnacle. Cuttlefish have an internal aragonite shell that serves as a structural support and a buoyancy control device[240]. The hard exoskeletons of crustaceans are formed from heavy deposits of $CaCO_3$. During the moult cycle, crustaceans conserve minerals by absorbing $CaCO_3$ from their shell before it is shed, into their blood stream in order to strengthen the new exoskeleton[241], at which time they are vulnerable to predation and disease.

A growing body of information is becoming available on the effects of increasing CO_2 on shallow-water marine benthos. Recent studies have investigated the physiological and calcification effects of long-term exposure (3–6 months) of molluscs and sea urchins to high CO_2 environments, and results suggest that an increase in atmospheric CO_2 of 200 ppm would have significant implications for the physiology of certain species, and is dependent on the internal pH regulation mechanisms[242]. Specimens of the mussel *Mytilus galloprovincialis*[243] and sea urchins *Hemicentrotus pulcherrimus* and *Echinometra mathaei* demonstrated a significant reduction in growth rate, size and body weights, and shell dissolution when exposed to low pH[244]. Calcification rates in *Mytilus edulis* were observed to decline linearly with increasing CO_2 levels, and 70% of oyster *Crassostrea gigas* larvae reared under pH 7.4 were either

237 Guinotte, J. M., Orr, J., Cairns, S., Freiwald, A., Morgan, L., George, R. (2006). Will human-induced changes in seawater chemistry alter the distribution of deep-sea scleractinian corals? Front Ecol Environ 4(3):141–146.

238 Maier, C., Hegeman, J., Weinbauer, M. G., Gattuso, J.-P. (2009). Calcification of the cold-water coral *Lophelia pertusa under* ambient and reduced pH. Biogeosciences, 6: 1671–1680.

239 The Royal Society (2005). Ocean Acidification due to increasing atmospheric carbon dioxide. Policy Document 12/05. http://royalsociety.org/document.asp?id=3249

240 Gutowska, M., Portner, H. O., Melzner, F. (2008). Growth and calcification in the cephalopod Sepia officinalis under elevated seawater pCO_2. Mar Ecol Prog Ser 373:303–309.

241 Pechenik, J. A. (2000). *Biology of the Invertebrates,* 4th ed. Boston: McGraw-Hill http://www.biologyreference.com/Co-Dn/Crustacean.html#ixzz0W5s4vpmJ

242 Shirayama, Y., Thornton, H. (2005). Effect of increased atmospheric CO_2 on shallow water marine benthos. Journal of Geophysical Research, Vol, 110:C09S08.

243 Michaelidis, B., Ouzounis, C., Paleras, A., Portner, H. O. (2005). Effects of long-term moderate hypercapnia on acid-base balance and growth rate in marine mussels *Mytilus galloprovincialis*. Mar Ecol Prog Ser 293:109–118.

244 Shirayama, Y., Thornton, H. (2005). Effect of increased atmospheric CO_2 on shallow water marine benthos. Journal of Geophysical Research, Vol, 110:C09S08

completely non-shelled, or only partially shelled, in contrast to 70% successful development in control embryos[245]. Additionally, a 40% reduction in sperm mobility of *C. gigas* was observed in response to large pH changes from pH8 to pH6. However, this is beyond any expected change in pH in the oceans due to increases in CO_2 concentrations in the near future[246].

M. edulis possesses strong physiological mechanisms by which it is able to protect body tissues against short-term exposure to highly acidified seawater. However, these mechanisms come at an energetic cost, which can result in reduced growth during long-term exposures. The medium-term (32 days) exposure of *M. edulis* to elevated CO_2 levels disrupted important immune responses and significantly reduced organism health by suppressing levels of phagocytosis[247] and elevating levels of calcium ions in the haemolymph following the dissolution of the $CaCO_3$ shells. Consequently, the predicted long-term changes to seawater chemistry associated with ocean acidification are likely to have a significant effect on the health and survival of *M. edulis* populations[248]. Mussel beds are a dominant coastal habitat along the northeastern Pacific and northwestern Atlantic, and, in general are an important habitat on most temperate rocky shores, providing food and structure for a diverse array of species in an otherwise physically stressful environment.

Significant reductions (25%) in sperm swimming speed, motility and reproduction success were observed within the sea urchin *Heliocidaris erythrogramma* following exposure to CO_2-induced acidification by 0.4 units, the upper limit of the IPCC predictions for 2100[249]. A delay in the developmental rate was also observed to increase mortality of embryos during the planktonic period, due to predation[250]. However, *H. erythrogramma* fertilization and early development were observed during one study to be robust to decreased pH within predicted values for environmental change, but sensitive to temperature, which caused developmental failure. This is due in part to the naturally low pH associated with urchin fertilization (pH 7.6), and possible adaptations of this species to a broad range of pH characteristic of intertidal habitats. This suggests that sea urchin embryos may not reach the calcifying stage in a warm ocean and emphasizes the need for experiments that concurrently address the two main stressors set to change the global oceans: temperature and acidification[251]. While the mechanism of these effects remains poorly understood, these findings have important implications for the reproductive and population viability of broadcast spawning marine species in a future acidified and warmer ocean. Furthermore, sea urchin tests are made of magnesium calcite, which is substantially more soluble than calcite, and their morphology facilitates direct contact between the internal body cavity and ambient seawater, leading them to be more sensitive to CO_2-associated pH decreases[252].

Exposure of the brittlestar *Ophiothrix fragilis* to low pH resulted in a temporal decrease in larval size as well as abnormal development and skeletogenesis. Acidification of 0.2 units induced 100% larval

245 Kurihara, H. (2008). Effects of CO_2 driven ocean acidification on the early developmental stages of invertebrates. Mar Ecol Prog Ser, Vol. 373:275–284.

246 The Royal Society (2005). Ocean Acidification due to increasing atmospheric carbon dioxide. Policy Document 12/05. http://royalsociety.org/document.asp?id=3249

247 Bibby, R., Widdicombe, S., Parry, H., Spicer, J., Pipe, R. (2008). Effects of ocean acidification on the immune response of the blue mussel *Mytilus edulis*. Aquatic Biology. Vol, 2:67–74.

248 Beesley, A., Lowe, D. M., Pascoe, C.K., Widdicombe, S. (2008). Effects of CO_2-induced seawater acidification on the health of *Mytilus edulis*. Climate Research, Vol. 37:215–225.

249 Havenhand, J. N., Buttler, F. R., Thorndyke, M. C., Williamson, J. E. (2008). Near-future levels of ocean acidification reduce fertilization success in a sea urchin. Current Biology. Vol, 18(5):651–652.

250 Kurihara, H., Shirayama, Y. (2004). Effects of increased atmospheric CO_2 on sea urchin early development. Mar Ecol Prog Ser. Vol 274:161–169.

251 Byrne, M., Ho, M., Selvakumaraswamy, P., Nguyen, H. D., Dworjanyn, S. A., Davis, A. R. (2009). Temperature, but not pH, compromises sea urchin fertilization and early development under near future climate change scenarios. Proc. R. Soc. B. 276:1883–1888.

252 Shirayama, Y., Thornton, H. (2005). Effect of increased atmospheric CO_2 on shallow water marine benthos. Journal of Geophysical Research, Vol, 110:C09S08

mortality within an eight-day period. Control larvae showed 70% survival over the same period. The calcite skeleton of the larval brittlestar has been proposed to aid key functions such as feeding and vertical migration, and defense against predators. Abnormal development of the skeleton would therefore be expected to have dramatic consequences for fitness. *Ophiothrix fragilis*, a keystone species, occur in high densities and stable populations through the shelf seas of the eastern Atlantic[253]. The burrowing ophiuroid *Amphiura filiformis* plays an important role in nutrient cycling through bioturbation and burrow-irrigation activities in sediments. Physiological changes to *Amphiura filiformis* as a result of a CO_2 exposure study affected nitrate fluxes by changing the irrigation activities, either through an increased demand for oxygen or food, or by muscle wastage that reduces the capacity to bioirrigate. This study suggests that ocean acidification-related impairment of organisms can affect the relationships between the key components driving ecosystem function[254].

A study to investigate the synergistic effects of ocean acidification and temperature on the fertilization and embryonic development of the economically and ecologically important Sydney rock oyster (*Saccostrea glomerata*) demonstrated that both pCO_2 increases and temperature deviation from the optimum for fertilization (26°C) reduced fertilization significantly. Prolonged exposure of elevated pCO_2 and temperature across early developmental stages led to fewer D-veliger (shelled) larvae, more abnormality and smaller sizes in elevated CO_2 environments and may lead to lethal effects at suboptimal temperatures[255].

Early life stages of organisms appear to be more sensitive to environmental disturbances than adults[256]. For example, juveniles of two snail species in Ischia, a naturally acidified site, were absent in areas with a minimum pH of 7.4, and the shells of adult specimens were severely corroded and weakened by the acidified sea water, an effect which probably increases their risk of predation (Figure 14) [257]. Investigations into the effects of ocean acidification on developing embryos of the intertidal gastropod, *Littorina obtusata* demonstrated slower overall development time, altered embryonic movement, and modification of shell shape in hatchlings, suggesting that ocean acidification may affect embryonic marine organisms in subtle but significant ways[258].

These results are in contrast to one recent study of the effects of ocean acidification over the life history of the barnacle *Amphibalanus Amphitrite,* which observed no effects of reduced pH on larval condition, cyprid (final larval stage) size, cyprid attachment and metamorphosis, juvenile to adult growth, or egg production. Nonetheless, barnacles exposed to the CO_2-driven acidification of seawater down to a pH of 7.4 displayed a trend of larger basal shell diameters during growth, suggestive of compensatory calcification. Furthermore, greater force was required to cause shell breakage of adults raised at pH 7.4, indicating that the lower, active growth regions of the wall shells had become more heavily calcified[259].

253 Dupont S., Havenhand J., Thorndyke W., Peck L. & Thorndyke M., 2008. Near-future level of CO_2-driven ocean acidification radically affects larval survival and development in the brittlestar *Ophiothrix fragilis. Marine Ecology Progress Series* 373:285–294

254 Wood, H. L., Spicer, J. I., Widdicombe, S. (2008). Ocean acidification may increase calcification – but at a cost. Proc. R. Soc. Lond. B – Biol. Sci., 275(1644):1767–1773.

255 Parker, L. M., P. M. Ross, and W. A. O'Connor (2009), The effect of ocean acidification and temperature on the fertilization and embryonic development of the Sydney rock oyster *Saccostrea glomerata* (Gould 1850), Global Change Biology, 15(9), 2123–2136, doi:10.1111/j.1365–2486.2009.01895.x.

256 Gazeau, F., Quiblier, C., Jansen, J., Gattuso, J. P., Middleburg, J., Heip, C. (2007). Impact of elevated CO_2 on shellfish calcification. *Geophys Res Lett* 34:L07603.

257 Hall-Spencer, J. M., Rodolfo-Metalpa, R., Martin, S., Ransome, E., Fine, M., Turner, S. M., Rowley, S. J., Tedesco, D., Buia, M. C. (2008). Volcanic carbon dioxide vents show ecosystem effects of ocean acidification. *Nature* 454:96–99.

258 Ellis, R. P., Bersey, J., Rundle, S., Hall-Spencer, J. M., Spicer, J. I. (2009). Subtle but significant effects of CO_2 acidified seawater on embryos of the intertidal snail, Littorina obtusata. *Aquat Biol* 5:41–018.

259 McDonald, M. R., McClintock, J. B., Amsler, C. D., Rittschof, D., Angus, R. A., Orihuela, B., Lutostanski, K. (2008). Effects of ocean acidification over the life history of the barnacle Amphibalanus Amphitrite. *Mar Ecol Prog Ser* 385:179–187.

FIGURE 14: *P. caerulea* and *H. truculus* showing severely eroded, pitted shells in naturally acidified areas of minimum pH 7.4. *Source: Hall-Spencer, 2008*[260].

A study of the active cephalopod mollusc *Sepia officinalis* demonstrated that this invertebrate is capable of not only maintaining calcification, but also growth rates and metabolism when exposed to elevated partial pressures of carbon dioxide (pCO_2). During a six-week experimentation period, juvenile *S. officinalis* maintained calcification rates under ~4,000 and ~6,000 ppm CO_2 and grew at the same rate with the same gross growth efficiency as control animals. They gained approximately 4% body mass daily and increased the mass of their calcified cuttlebone by over 500%. The study concluded that active cephalopods possess a certain level of pre-adaptation to long-term increments in carbon dioxide levels[261].

Culture of the early larval stages of an economically important crustacean, the European lobster *Homarus gammaru* in CO_2-acidified sea water led to a reduction in carapace mass during the final stage of larval development. A reduction in exoskeletal mineral (calcium and magnesium) content of the carapace was observed concurrently, despite treatment waters being saturated with respect to the calcium carbonate polymorphs measured. The physiological alterations recorded were attributed to acidosis or hypercapnia interfering with normal homeostatic function. Despite there being no observed effect on survival, carapace length, or zoeal (larval stage) progression, the indirect disruption of calcification and carapace mass by ocean acidification may still adversely affect the competitive fitness and recruitment success of larval lobsters with serious consequences for population dynamics and marine ecosystem function[262].

D. PELAGIC COMMUNITIES

Calcified organisms are significant components of pelagic ecosystems, occupying the base of the marine food chain, accounting for the majority of the organic carbon used by organisms in mid and deep-water layers of the oceans, and playing an important role, in the interactions of the surface oceans with the atmosphere, such as in the exchange of CO_2[263]. Any changes in the functioning of these organisms as a result of ocean acidification could have significant consequences for ecosystem functioning. Changes to the biological pump and therefore the flux of particulate organic matter from overlying waters to benthic communities has the potential to significantly alter the cycling of nutrients between the bottom sediments and overlying water column. Table 3 summarizes the key pelagic groups, the role or influence of $CaCO_3$, and the observed impacts and implications of exposure to elevated CO_2 and decreasing pH.

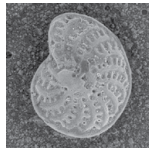
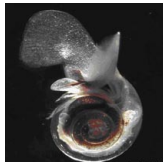
260 Hall-Spencer, J. M., Rodolfo-Metalpa, R., Martin, S., Ransome, E., Fine, M., Turner, S. M., Rowley, S. J., Tedesco, D., Buia, M. C. (2008). Volcanic carbon dioxide vents show ecosystem effects of ocean acidification. *Nature* 454:96–99.

261 Gutowska, M., Portner, H. O., Melzner, F. (2008). Growth and calcification in the cephalopod Sepia officinalis under elevated seawater pCO_2. *Mar Ecol Prog Ser* 373:303–309.

262 Arnold, K. E., Findlay, H. S., Spicer, J. I., Daniels, C. L., & Boothroyd, D., 2009. Effect of CO_2-related acidification on aspects of the larval development of the European lobster, Homarus gammarus (L.). *Biogeosciences* 6(8): 1747–1754.

263 The Royal Society (2005). Ocean Acidification due to increasing atmospheric carbon dioxide. Policy Document 12/05. http://royalsociety.org/document.asp?id=3249

TABLE 3: Summary of observed and predicted (*) impacts of high CO_2 and ocean acidification on pelagic marine organisms.

Organism	Function of $CaCO_3$	Observed impacts of elevated CO_2	Observed impacts of low pH	Socio-ecological implications
Foraminifera  (Image: UCMP)	Mechanical protection	Reduction in shell mass in foraminifera *Orbulina universa* 4–8% and *Globigerinoides sacculifer* 6–14% [264] in increased pCO_2 conditions;	30–35% reduction in shell mass since the pre-industrial Holocene in *Globigerina bulloides*[265] Lighter, thin-walled shells observed in younger planktonic foraminifera *Globigerinoides ruger* from surface sediments compared to shells found deeper in the sediment[266].	Produce the majority of pelagic $CaCO_3$ on a global basis[267]
Pteropods  (Image: NOAA)	Mechanical protection		28% reduction in calcification observed in *Limacina helicina* in response to decreasing pH observed at the pH value expected for 2100 compared to present pH[268]. Pteropods, *Clio pyramidata*, from the subarctic Pacific that were exposed to aragonite under-saturation similar to that projected for the surface waters of the Southern Ocean by 2100 experienced shell dissolution within 48 hours[269].	Loss of food source for key marine predators – Mackerel, Salmon[270];
Coccolithophores (Image: Celsias)	Structural calcite plates	40% decrease in calcification rates observed in *Emiliania huxleyi* with increasing pCO_2[271]. No significant change observed in *Coccolithus pelagicus* in response to elevated pCO_2.[272] Initial increase in calcification rate of *Calcidiscus leptoporus* followed by a decrease[273]. A doubling of cell-specific calcification rates for *E. Huxleyi* observed at 750µatm compared to 300µatm pCO_2[274].		Shift in phytoplankton community structure; Potential for variations in elemental stochiometry in cells as a result of increased pCO_2 which is known to influence food selection by second trophic level grazers[275]. Blooms support the global albedo effect by up to 0.13%, reflecting sunlight back into space[276]. Production of Dimethylsulphide reduces the radiative flux to the Earth's surface

Organism	Function of $CaCO_3$	Observed impacts of elevated CO_2	Observed impacts of low pH	Socio-ecological implications
Marine fish, invertebrates and marine mammals		Adult Japanese amberjack, *Seriola quinqueradiata*, and bastard halibut, *Paralichthys olivaceus*, died within 8 and 48 h, respectively, during exposure to seawater equilibrated with 5% CO_2.[277] Deep-sea crab *Chionoecetes tanneri*, unable to regulate extracellular pH in response to (24 hour) increased pCO_2, In contrast, shallow living crab *Cancer magister* fully recovered its hemolymph pH[278]. Increased energy budget due to acid-base regulation and cardiorespiratory control in fish[279] Enhanced calcification in aragonite ear bones (otoliths) of fish *Atractoscion nobilis* grown in seawater with high pCO_2 (993 and 2558 µatm of CO_2)[280]	Protracted embryonic development[281]; Reduced ability of clownfish *Amphiprion percula* larvae to detect olfactory settlement cues when reared at levels of ocean pH 7.8[282]. CO_2-enriched seawater more toxic to eggs and larvae of marine fish silver seabream, *Pagrus major*, than HCl-acidified seawater when tested at the same seawater pH[283].	Juveniles and early development stages more susceptible, leading to reduced population size and ecosystem structure changes[284]; Little evidence of respiratory acclimation in marine fish[285]; Seagrass ecosystems may benefit from enhanced pCO_2 providing critical habitat for marine mammals. Eelgrass *Zostera marina* increased in biomass and reproductive output[286]

264 Bijma, J., Honisch, B., Zeebe, R. E. (2002). The 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. Geosyst. 3: 1064.

265 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.

266 de Moel, H., Ganssen, G. M., Peeters, F. J. C., Jung, S. J. A., Kroon, D., Brummer, G. J. A., & Zeebe, R. E., 2009. Planktic foraminiferal shell thinning in the Arabian Sea due to anthropogenic ocean acidification? Biogeosciences 6(9): 1917–1925

267 Fabry, V. J., Seibel, B. A., Freely, R. A., Orr, J. C. (2008). Impacts of ocean acidification on marine fauna and ecosystem processes. ICES Journal of Marine Science, 65:414–432.

268 Comeau, S., Gorsky, G., Jeffree, R., Teyssié, J.-L., and Gattuso, J.-P. (2009) Key Arctic pelagic mollusc (Limacina helicina) threatened by ocean acidification, Biogeosciences Discuss., 6, 2523–2537.

269 Guinotte, J. M., Fabry, V. J. (2008). Ocean acidification and its potential effects on marine ecosystems. Ann. N. Y. Acad. Sci. 1134: 320.

270 Fabry, V. J., Seibel, B. A., Feely, R. A., Orr, J. C. (2008). Impacts of ocean acidification on marine fauna and ecosystem processes. ICES Journal of Marine Science, 65:414–432.

271 Wolf-Gladrow, D. A., Riebesell, U., Burkhardt, S., Bjima, J. (1999). Direct effects of CO_2 concentration on growth and isotopic composition of marine plankton. Tellus 51B:461–476.

272 Langer, M. R., *et al.* (2006). Species-specific responses of calcifying organisms to changing seawater carbonate chemistry. Geochemistry Geophysics Geosystems. 7:np.

273 Langer G., Geisen M., Baumann K.H., Kläs J., Riebesell U., Thoms S. and Young J.R., 2006. Species – specific responses of calcifying algae to changing seawater carbonate chemistry. Geochem. Geophys. Geosyst., 7(9): 1–12.

274 Iglesias-Rodriguez, M. D., Halloran, P. R., Rickaby, R. E. M., Hall, I. R., Colmenero-Hidalgo, E., Gittins, J. R., Green, D. R. H., Tyrell, T., Gibbs, S. J., von Dassow, P., Rehm, E., Armbrust, E. V., Boessenkool, K. P. (2008). Phytoplankton Calcification in a High-CO_2 World. Science, 320:336–340.

275 Engel A., Zondervan I., Aerts K., Beaufort L., Benthien A., Chou L., Delille B., Gattuso J.P., Harlay J., Heemann C., Hoffmann L., Jacquet S., Nejstgaard J., Pizay M.D., Rochelle-Newall E., Schneider U., Terbrueggen A. and Riebesell U., 2005. Testing the direct effect of CO2 concentration on a bloom of the coccolithophorid Emiliania huxleyi in mesocosm experiments. Limnol. Oceangr., 50: 493–507.

276 The Royal Society (2005). Ocean Acidification due to increasing atmospheric carbon dioxide. Policy Document 12/05. http://royalsociety.org/document.asp?id=3249

277 Ishimatsu, A., Kikkawa, T., Hayashi, M., Lee, K. S. (2004) Effects of CO_2 on Marine Fish: Larvae and Adults. Journal of Oceanography 60:731–741.

278 Pane, E. F., Barry, J. P. (2007). Extracellular acid-base regulation during short term hypercapnia is effective in a shallow-water crab, but ineffective in a deep sea crab. Mar Ecol Prog Ser 334:1–9.

279 Ishimatsu, A., Hayashi, M., Kikkawa, T. (2008) Fishes in high CO_2 acidified oceans. Mar Ecol Prog Ser, Vol 373:295–302.

280 Checkley Jr., D. M., Dickson, A. G., Takahashi, M., Radich, J. A., Eisenkolb, N., Asch, R. (2009). Elevated CO_2 enhances otolith growth in young fish. Science 324: 1683.

281 Egilsdottir, H., Spicer, J. I. & Rundle, S. D., in press. The effect of CO_2 acidified sea water and reduced salinity on aspects of the embryonic development of the amphipod Echinogammarus marinus (Leach). Marine Pollution Bulletin in press.

282 Munday, P.L., S.L. Dixson, J.M. Donelson, G.P. Jones, M.S. Pratchett, G.V. Devitsina, and K.B. Doving 2009. Ocean acidification impairs olfactory discrimination and homing ability of a marine fish. Proceedings of the National Academy of Sciences. 106 (6) 1848–1852

283 Ishimatsu, A., Kikkawa, T., Hayashi, M., Lee, K. S. (2004) Effects of CO_2 on Marine Fish: Larvae and Adults. Journal of Oceanography 60:731–741.

284 Ibid.

285 Ishimatsu, A., Hayashi, M., Kikkawa, T. (2008) Fishes in high CO_2 acidified oceans. Mar Ecol Prog Ser, Vol 373:295–302.

286 Palacios, S., Zimmerman, R. C. (2007). Response of eelgrass Zostera marina to CO_2 enrichment: possible impacts of climate change and potential for remediation of coastal habitats. Mar Ecol Prog Ser, 344:1–13.

Foraminifera and Pteropods

Both planktonic foraminifera and pteropods are important components of polar and sub-polar ecosystems, providing a food source for marine predators, including North Pacific salmon, mackerel, herring, cod and baleen whales[287]. Pteropods are the dominant calcifier in the Southern Ocean and can reach densities ofthousands to greater than 10,000 individuals m^{-3} in high-latitude areas. Data from the Southern Ocean show that planktonic foraminifera are already demonstrating reduced calcification, consistent with laboratory experiments and the degree of calcite saturation reduction measurable in the Southern Ocean[288]. This study is the first field evidence for a reduction in calcification in nature in response to ocean acidification. These findings are supported by an investigation into the effects of anthropogenic ocean acidification on shell weights and wall thickness of the planktonic foraminifer *Globigerinoides ruber* in the Western Arabian Sea. However, the authors of the latter study suggest that a scenario with seasonal production of thick and thin shells could also explain the observed changes in shell weight and wall thickness[289]. A companion study on pteropod calcification shows a high degree of inter-annual variability but sets a baseline for detecting future acidification impacts on these pelagic molluscs[290].

Live pteropods, *Clio pyramidata*, from the subarctic Pacific that were exposed through laboratory experiments to a level of aragonite under-saturation similar to that projected for the surface waters of the Southern Ocean by the end of the century, experienced shell dissolution within 48 hours, even though animals were actively swimming[291]. The impact of changes in the carbonate chemistry was investigated recently on the pteropod *Limacina helicina*, a key species of Arctic ecosystems. The pteropods were kept in culture under controlled pH conditions corresponding to pCO_2 levels of 350 and 760 μatm. A 28% decrease in calcification was observed at the pH value expected for 2100 compared to the present pH value[292].

When grown in laboratory experiments in seawater equivalent to pCO_2 values of 560 and 740 ppmv, the shell mass of foraminifera *Orbulina univera* and *Globigerinoides saccuifer* declined by 4–8% and 6–14% respectively, compared to the shell mass secreted at the preindustrial pCO_2 value[293]. Though both groups have proved difficult to grow in laboratory culture, data suggest that both groups reduce calcification in response to ocean acidification, however the small number of species studied precludes the extrapolation of general trends. Pteropods produce $CaCO_3$ in its aragonite form, and thus are likely to be particularly sensitive to ocean acidification, more so than coccolithophores and foraminifera, which produce less soluble calcite[294].

287 Fabry, V. J., Seibel, B. A., Freely, R. A., Orr, J. C. (2008). Impacts of ocean acidification on marine fauna and ecosystem processes. *ICES Journal of Marine Science* 65:414–432.

288 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

289 de Moel, H., Ganssen, G. M., Peeters, F. J. C., Jung, S. J. A., Kroon, D., Brummer, G. J. A., & Zeebe, R. E., 2009. Planktic foraminiferal shell thinning in the Arabian Sea due to anthropogenic ocean acidification? *Biogeosciences* 6(9): 1917–1925.

290 Roberts, D., Howard, W. R., Moy, A. D., Roberts, J. L., Trull, T. W., Bray, S. G, and Hopcroft, R. R. (2008). Interannual variability of pteropod shell weights in the high-CO_2 Southern Ocean, *Biogeosciences Discuss.*, 5(6), 4453–4480

291 Guinotte, J. M., Fabry, V. J. (2008). Ocean acidification and its potential effects on marine ecosystems. Ann. N. Y. Acad. Sci. 1134: 320.

292 Comeau, S., Gorsky, G., Jeffree, R., Teyssié, J.-L., and Gattuso, J.-P. (2009) Key Arctic pelagic mollusc (*Limacina helicina*) threatened by ocean acidification, Biogeosciences Discuss., 6, 2523–2537.

293 Bijma, J., Honisch, B., Zeebe, R. E. (2002). The 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. Geosyst. 3: 1064.

294 The Royal Society (2005). Ocean Acidification due to increasing atmospheric carbon dioxide. Policy Document 12/05. http://royalsociety.org/document.asp?id=3249

Coccolithophores

Coccolithophores are a dominant or common component of the phytoplankton community in the sunlit euphotic zone, distributed in accordance with areas of high calcite saturation. Coccolithophores secrete tests or plates made of calcite and can form massive blooms covering hundreds of thousands of square kilometres, significantly influencing the carbon cycle and seawater alkalinity[295]. These blooms can produce up to one million tonnes of calcite and are visible from satellites in temperate and sub-polar regions. There have been controversial results from culture experiments on the impact of increased CO_2 on coccolithophore calcification[296]. Decreasing rates of calcification of 40% have been observed in the coccolithophorid *Emiliania huxleyi* with increasing pCO_2[297], and up to 66% with pCO_2 values of 800ppm[15]. However, the majority of studies have focused on only this species of coccolithophore and variable results have been returned from observations of *Coccolithus pelagicus,* which did not demonstrate a significant change in calcification rates with increased CO_2[298].

Experimental evidence suggests large variation in the CO_2 requirements, sensitivity and metabolism of phytoplankton taxonomic groups and highlights that some groups such as calcifying coccolithophorids, may benefit more from the present increase in atmospheric CO_2 compared to non-calcifying diatoms[299]. *Emiliania huxleyi,* for example, generally exhibits an increase in photosynthetic rates in response to elevated CO_2 levels in both laboratory studies and natural communities. However, a reduction in the degree of calcification as a result of increasing acidification is assumed to put coccolithophores at an ecological disadvantage in future oceans[300].

Large vertical gradients in environmental variables exist in the upper 1000m ,and most zooplankton migrate daily from near-surface water depths to depths of 200–700m. These migrations expose zooplankton to wide variations in pCO_2, values greater than those expected for average surface waters as a result of anthropogenic acidification over the next 100 years. Therefore, vertically migrating species, like those living intertidally or near hydrothermal vents, experience oscillating periods of simultaneous hypoxia and high pCO_2 that require specific adaptation for tolerance. These species may be more tolerant of elevated pCO_2, at least on short time scales, than those in well-oxygenated regions. However, there is no evidence that adaptation to this variability promotes tolerance of chronic ocean acidification such as that expected over the next century[301].

Marine Fish and Marine Mammals

In addition to using $CaCO_3$ for strengthening skeletal structures, the use of calcium minerals in gravity sensory organs is widespread among ocean fauna, with, for example, an active role in the motor neural programme that underlies search movements for prey during hunting behaviour[302]. In squid and fish for example, these organs are composed of aragonite.

295 Rost, B., Zondervan, I., Wolf-Gladrow, D. (200*) Sensitivity of phytoplankton to future changes in ocean carbonate chemistry: current knowledge, contradictions and research directions. Mar Ecol Prog Ser, Vol. 373:227–237.

296 CIESM, 2008. Impacts of acidification on biological, chemical and physical systems in the Mediterranean and Black Seas. N° 36 in *CIESM Workshop Monographs* [F. Briand Ed.], 124 pages, Monaco

297 Wolf-Gladrow, D. A., Riebesell, U., Burkhardt, S., Bjima, J. (1999). Direct effects of CO_2 concentration on growth and isotopic composition of marine plankton. Tellus 51B:461–476.

298 Langer, M. R., *et al.* (2006). Species-specific responses of calcifying organisms to changing seawater carbonate chemistry. Geochemistry Geophysics Geosystems. 7:np.

299 Riebesell, U. (2004). Effects of CO_2 enrichment on Marine Phytoplankton. Journal of Oceanography, Vol 60:719–729.

300 Rost, B., Zondervan, I., Wolf-Gladrow, D. (200*) Sensitivity of phytoplankton to future changes in ocean carbonate chemistry: current knowledge, contradictions and research directions. Mar Ecol Prog Ser, Vol. 373:227–237.

301 Fabry, V. J., Seibel, B. A., Feely, R. A., Orr, J. C. (2008). Impacts of ocean acidification on marine fauna and ecosystem processes. *ICES Journal of Marine Science* 65:414–432

302 Ibid.

When pCO_2 levels increase in seawater, dissolved CO_2 more readily diffuses across animal surfaces and cellular spaces, causing pH levels to decrease. Acidification of the body tissues (acidosis), which can occur in a matter of hours in fish and invertebrates, reduces the oxygen carrying capacity of the blood, and is shown to reduce cellular energy and lower respiratory activity[303]. Evidence is also available of longer term effects, including lower rates of protein synthesis affecting growth and reproduction functions. Fish in early developmental stages are more susceptible to environmental toxicants than adults, leading to a gradual reduction in population sizes and changes to ecosystem structures[304].

Accumulating evidence for reef fishes suggest that both reef sounds and olfactory cues are used by larvae to locate appropriate adult reef habitat at the end of their pelagic phase. An investigation into the effects of CO_2-driven ocean acidification on the ability of settlement stage clownfish *Amphiprion percula* larvae to detect olfactory cues (e.g. anemones, parents, leaves) revealed that larvae became strongly attracted to olfactory cues that they would normally avoid when reared at levels of ocean pH 7.8. Furthermore, larvae no longer responded to any olfactory cues when reared at pH 7.6. These results suggest that the elevated pCO_2 conditions that could occur in the world's oceans early next century can dramatically affect the behavioural decisions of marine organisms during critical stages of their life history[305].

Elevations of ambient pCO_2 may require fishes to spend more energy for physiological adaptations, in particular acid-base regulation and cardio-respiratory control. The cost of osmoregulation in seawater fish is estimated to be 6–15% of resting oxygen consumption, and an elevation in pCO_2 would require additional energy expenditure on top of this baseline. There is little evidence that fish would show respiratory acclimation during long-term exposure to a high pCO_2 environment[306].

Most studies have shown a slowing of structural calcification under enhanced pCO_2[307]. However, in a recent experiment, the eggs and pre-feeding larvae of the white sea bass (*Atractoscion nobilis*) were grown in seawater with high pCO_2 to determine the influence on bony aragonite-protein structures used by fish to sense orientation and acceleration (otoliths). Contrary to expectations, the otoliths of fish grown in seawater with high pCO_2 (993 and 2558 µatm of CO_2), and therefore lower pH and aragonite saturation state, had significantly larger otoliths than those of fish grown under simulations of present-day conditions (380 µatm of CO_2). The results are consistent with young fish being able to control the concentration of ions (H^+ and Ca^{2+}), but not the neutral molecule CO_2, in the endolymph surrounding the otolith. It is not known whether these results apply to other taxa with aragonite sensory organs, such as squid and mysids (statoliths) or other fish species. Nor is it known if larger otoliths have a deleterious effect, although it is understood that asymmetry between otoliths can be harmful[308].

Laboratory studies to assess the short-term tolerance of the deep-sea Tanner crab *Chionoecetes tanneri* to increased pCO_2, revealed that this species is unable to regulate extracellular pH during short-term (24-hour) CO_2 exposure. In contrast, *Cancer magister*, a shallow-living crab, fully recovered its hemolymph (blood analogue in arthropods) pH over 24 hours of elevated pCO_2 (hypercapnia) exposure through the net accumulation of bicarbonate from the surrounding medium. These results support

303 Ibid.

304 Ishimatsu, A., Kikkawa, T., Hayashi, M., Lee, K. S. (2004) Effects of CO_2 on Marine Fish: Larvae and Adults. *Journal of Oceanography* 60:731–741.

305 Munday, P.L., S.L. Dixson, J.M. Donelson, G.P. Jones, M.S. Pratchett, G.V. Devitsina, and K.B. Doving 2009. Ocean acidification impairs olfactory discrimination and homing ability of a marine fish. Proceedings *of the National Academy of Sciences*. 106 (6) 1848–1852.

306 Ishimatsu, A., Hayashi, M., Kikkawa, T. (2008) Fishes in high CO_2 acidified oceans. Mar Ecol Prog Ser, Vol 373:295–302.

307 Doney, S. C., Fabry, V. J., Feely, R. A., Kleypas, J. A. (2009). Ocean Acidification: The Other CO_2 problem. *Annu. Rev. Mar. Sci.* 1:169–192.

308 Checkley Jr., D. M., Dickson, A. G., Takahashi, M., Radich, J. A., Eisenkolb, N., Asch, R. (2009). Elevated CO_2 enhances otolith growth in young fish. *Science* 324: 1683.

the hypothesis that hypercapnia will have a profound physiological impact on deep-sea organisms that exhibit reduced metabolic rates and lack the short-term acid base regulatory capacity to cope with acute hypercapnic stress[309].

Several higher order and endangered marine mammals rely on seagrasses for a significant portion of their diet (e.g. dugongs, manatees). Seagrass ecosystems may be one of the few ecosystems to benefit from increasing pCO_2 in seawater[310]. In experiments with the eelgrass *Zostera marina,* an increase in biomass and reproductive output is reported under high CO_2 conditions, suggesting potentially higher productivity of critical seagrass habitat[311].

E. ECOLOGICAL CONSEQUENCES

Ocean acidification is expected to have major negative impacts on corals and other marine organisms that build $CaCO_3$ skeletons and shells, and whose success is largely controlled by carbonate chemistry. Many calcifying species are located at the bottom or middle of global ocean food webs, therefore loss of shelled organisms to ocean acidification will alter predator–prey relationships and the effects will be transmitted throughout the ecosystem[312]. In addition to the likely disruptions through large components of the marine food web, a loss or change in biodiversity could have significant ecological consequences[313].

The shoaling of the saturation horizon for aragonite and calcite has implications for calcifying organisms across the globe, which form a significant component of pelagic and benthic ecosystems. The concern is especially high in polar regions, where saturation states are naturally low. The reduction and possibly regional cessation of calcification by organisms in the oceans would strongly affect ecosystem regulation and the flow of organic material to the seafloor, through the removal of $CaCO_3$ mineral ballast and the reduced efficiency of the biological pump to transfer carbon into the ocean interior[314, 315].

The global standing stock of particulate inorganic carbon (PIC) depends on calcium carbonate production and dissolution, both of which will be affected by ocean acidification. A host of marine organisms contribute to PIC, which means that the combined effects of climate change and ocean acidification on PIC are hard to predict[316]. Experiments to date have not been undertaken over long enough time scales to demonstrate adaptation or evolution in existing species. However, any reduction in total biomass production either through reduced photosynthesis or from greater energy demand to obtain critical nutrients will have significant implications for global marine food webs. The foodweb of polar areas, such as the Beaufort Sea, demonstrates the complex interconnections that are at risk from ocean acidification (Figure 15).

309 Pane, E. F., Barry, J. P. (2007). Extracellular acid-base regulation during short term hypercapnia is effective in a shallow-water crab, but ineffective in a deep sea crab. *Mar Ecol Prog Ser*, 334:1–9.

310 Guinotte, J. M., Fabry, V. J. (2008). Ocean acidification and its potential effects on marine ecosystems. *Ann. N. Y. Acad. Sci.* 1134: 320.

311 Palacios, S., Zimmerman, R. C. (2007). Response of eelgrass *Zostera marina* to CO_2 enrichment: possible impacts of climate change and potential for remediation of coastal habitats. *Mar Ecol Prog Ser*, 344:1–13.

312 Cooley, S. R., Doney, S. C. (2009). Ocean Acidification's impact on Fisheries and Societies: A U.S Perspective. *Journal of Marine Education*, 25(1):15–19.

313 OSPAR Commission (2006). Effects of the marine environment of ocean acidification resulting from elevated levels of CO_2 in the atmosphere.

314 The Royal Society (2005). Ocean Acidification due to increasing atmospheric carbon dioxide. Policy Document 12/05. http://royalsociety.org/document.asp?id=3249

315 Wolf-Gladrow, D. A., Riebesell, U., Burkhardt, S., Bjima, J. (1999). Direct effects of CO_2 concentration on growth and isotopic composition of marine plankton. *Tellus* 51B:461–476.

316 Balch, W. M., Fabry, V. J. (2008) Ocean acidification: documenting its impact on calcifying phytoplankton at basin scales. *Mar Ecol Prog Ser* 373: 239–247.

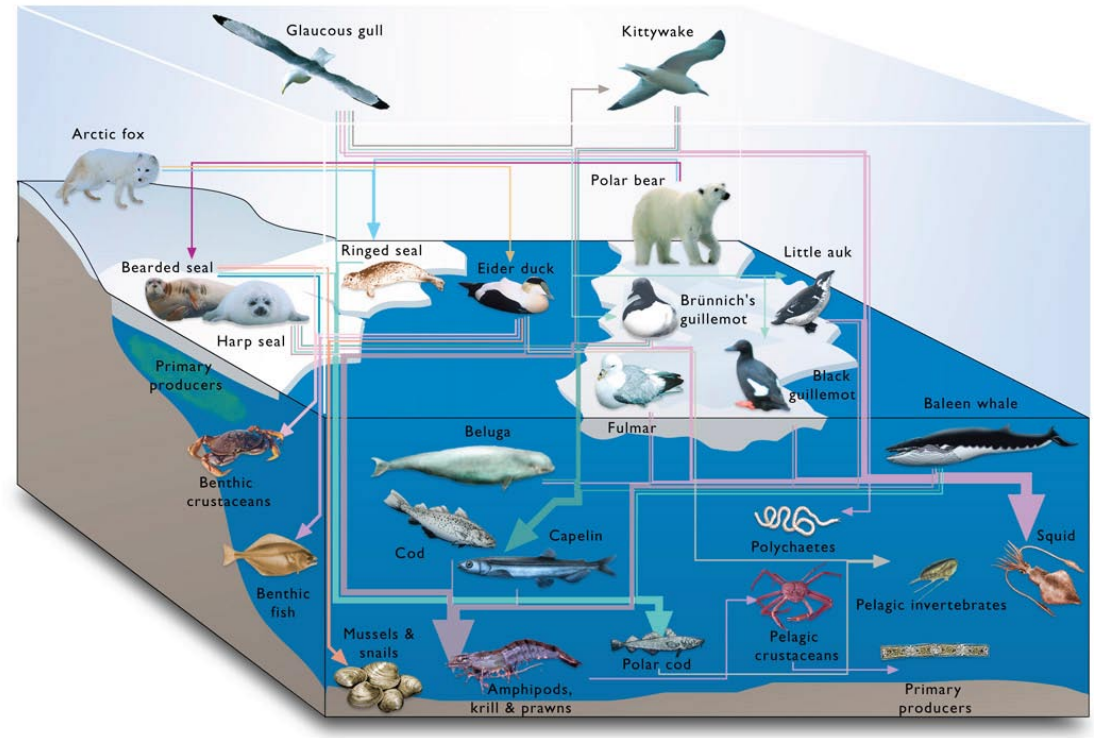


FIGURE 15: Trophic linkages in the Beaufort Sea. *Source: Arctic Climate Impacts Assessment (ACIA) Impacts of a Warming Arctic: Arctic Climate Impact Assessment. Cambridge University Press, 2007.*

Depth offers no protection from ocean acidification. Indeed, important cold-water coral communities will likely be the first casualties of increasing ocean acidity. In contrast to the contraction of tropical coral reefs towards the equator, it is the depth distribution of deep water coral communities that will contract; the deepest communities in each ocean will be the first to experience a shift from saturated to unsaturated conditions[317]. The predicted decline in carbonate saturation levels will severely affect cold-water corals and the continued provision of services such as shelter and food for hundreds of associated species, including commercial fish and shellfish. Many commercially exploited species rely on migration between deep and shallower waters at different life cycle stages. Furthermore, deep-sea organisms are responsible for almost the entire regeneration of nutrients in the oceans—without these processes the primary production in the photic zone of the oceans would collapse[318].

Calcified macroalgae (e.g. *Udotea, Amphiroa, Halimeda*) are distributed in marine habitats from polar to tropical latitudes and from intertidal shores to the deepest reaches of the euphotic zone. These algae play critical ecological roles, including being key to a range of invertebrate recruitment processes, functioning as ecosystem engineers through the provision of three-dimensional habitat structure, as well as contributing critical structural strength in coral reef ecosystems[319]. Calcified macroalgae contribute significantly to the deposition of carbonates in coastal environments. Calcifying macroalgae produce biogenic $CaCO_3$ in three forms: high-magnesium calcite, aragonite and calcite, all of which are susceptible

317 Doney, S. C., Fabry, V. J., Feely, R. A., Kleypas, J. A. (2009). Ocean Acidification: The Other CO_2 problem. *Annu. Rev. Mar. Sci.* 1:169–192.

318 UNEP. (2007). Deep-Sea Biodiversity and Ecosystems: A scoping report on their socio-economy, management and governance.

319 Nelson, W. A., 2009. Calcified macroalgae – critical to coastal ecosystems and vulnerable to change: a review. *Marine and Freshwater Research* 60(8): 787–801

to the negative effects of decreasing carbonate saturation states. Loss of this functional group would result in the subsequent loss of important habitat for adult fishes and invertebrates[320].

Calcifying pteropods are a key food for carnivorous zooplankton and fish. The decline of pteropod densities, as predicted for high latitude regions in the near future, will influence the predator-prey relationships of many species (e.g. cod, Pollock, haddock, mackerel) and could result in greater predation pressure on juvenile fish, such as salmon[321]. In contrast, species such as gymnosomes (unshelled pteropods), who prey exclusively on shelled pteropods would likely shift their geographic distribution in concert with their prey, assuming that both are able to overcome thermal tolerance limitations[322].

The mechanisms available to counteract acidification of body tissues are limited and conserved across animal phyla. Those species adapted to environments with steep CO_2 gradients, such as hydrothermal vents, and those species with high capacity for metabolic production of CO_2 have evolved greater capacities for buffering ion exchange and CO_2 transport[323]. However, whether such elevated capacity translates into greater tolerance to chronic ocean acidification is not known. The loss of key predators or grazing species from ecosystems could lead to environmental phase shifts (e.g. coral to algal-dominated reefs), or favour the proliferation of non-food organisms: a negative relationship between jellyfish abundance and ocean pH has been suggested for the western central North Sea, which will allow jellyfish to take advantage of vacant niches made available by the negative effects of acidification on calcifying plankton, although this has not been substantiated[324]. In some systems jellyfish are competitors and predators of fish and can replace fish as the dominant higher trophic level, negatively affecting commercial fish recruitment[325].

Evidence from a naturally acidified location confirms a reduced diversity among biological communities under-acidified seawater conditions. Around the CO_2 vents in Ischia, seagrasses and algae, including invasive species, dominate the marine community while species that rely on $CaCO_3$ to build their shells are completely absent. These observations provide valuable insight into the likely ecosystem-level impacts of ocean acidification[326].

Non-calcifying species are also affected through food web control and pH-dependent metabolic processes. Observations of two key marine photosynthetic cyanobacteria to warmer, more CO_2-rich revealed a variable physiological response reporting minimal influence for *Prochlorococcus*, but greatly elevated photosynthesis rates in *Synechococcus*[327]. Nitrogen-fixing cyanobacteria *Trichodesmium*, which support a large fraction of primary productivity in low nutrient areas of the world's oceans, show elevated rates of carbon and nitrogen fixation under increased pCO_2 conditions[328]. These results suggest that by the end of this century, elevated CO_2 could substantially increase global *Trichodesmium* N_2 and CO_2

320 Beck, M. W. *et al.* (2003). The role of nearshore ecosystems as fish and shellfish nurseries. Issues Ecol., 11:1–12.

321 Fabry, V. J., Seibel, B. A., Feely, R. A., Orr, J. C. (2008). Impacts of ocean acidification on marine fauna and ecosystem processes. ICES Journal of Marine Science, 65:414–432.

322 Ibid.

323 Ibid.

324 Richardson, A. J., Gibbons, M. J. (2008). Are jellyfish increasing in response to ocean acidification? Limnol Oceanogr. 53(5):2040–2045.

325 Purcell, J. E., Uye, S., Lo, W-T. (2007). Anthropogenic causes of jellyfish blooms and their direct consequences for humans. A Review. Mar Ecol Prog Ser, 350:153–174.

326 Hall-Spencer, J. M., Rauer, E. (2009) Assessing the ecological impacts of ocean acidification - from field observations to in situ experimentation. Journal of Marine Education, 25 (1): 11–12.

327 Fu, F. X., Warner, M. E., Zhang, Y., Feng, Y., Hutchins, D. A. (2007). Effects of increased temperature and CO_2 on photosynthesis, growth and elemental ratios of marine Synechococcus and Prochlorococcus (cyanobacteria). J. Phycol. 43:485–496.

328 Hutchins, D. A., Fe, F-X., Zhang, Y., Warner, M. E., Feng, Y., *et al.* (2007). CO_2 control of *Trichodesmium* N_2 fixation, photosynthesis, growth rates and elemental ratios: implications for past, present and future ocean biogeochemistry. Limnol. Oceanogr. 52(4):1293–1304.

fixation, fundamentally altering the current marine nitrogen and carbon cycles and potentially driving some oceanic regimes towards phosphate limitation. The abundance of fleshy algae (*Halosaccion glandiforme*), ephemeral algae, filamentous red algae, and foliose red algae have also been observed to increase with declining pH[329], suggesting that significant shifts in the community composition could be expected in future acidified oceans, with effects across the global marine food chain.

In order to accurately predict the consequences of ocean acidification for marine biodiversity and ecosystems, the ecological effects must be considered in relation to other environmental changes associated with global climate change, and the interplay between the complex biological and chemical feedbacks[330]. Surface water temperature is already increasing and predicted to increase further, while changes in rainfall and land runoff will impact salinity and nutrient input to coastal seas. The combined influences of increasing temperature, salinity and nutrient fluxes may increase the potential risk of hypoxia or anoxia in shelf sea systems[331]. Warming, the accumulation of CO_2 in surface layers and a decrease in oxygen content combine in their effects on marine fauna, depressing the aerobic capacity of organisms and resulting in a narrowing of thermal tolerances, which, under a climate gradient, will result in a decreasing range of bio-geographical distribution for organisms[332]. The negative interactions between temperature extremes and CO_2 are particularly acute in coral reefs. Even if the atmospheric CO_2 content stabilizes at 550ppm, these ecologically and economically important habitats will already be marginalized.

Significant feedback systems also stand to be influenced. Coccolithophore blooms have an albedo effect, reflecting significant amounts of sunlight back into space, which cannot then contribute to global warming. The loss of blooms could reduce the global albedo effect by up to 0.13%[333]. Additionally, coccolithophores are major producers of Dimethylsulphide (DMS), which, on release to the atmosphere, is oxidized to SO_4, an important component of aerosols, thought to influence the lifetimes and optical properties of clouds. DMS is supersaturated in surface waters, and emissions to the atmosphere by marine phytoplankton have been proposed to reduce the radiative flux to the Earth's surface[334]. The complex logistics of monitoring DMS cycling have prevented its effective characterization[335], however, it is clear that changes in the composition of the phytoplankton community would affect the size of this feedback to the global climate[336]. A shipboard incubation experiment was conducted to investigate the effects of increased temperature and pCO_2 on the algal community structure of the North Atlantic spring bloom, one of the largest annually occurring phytoplankton blooms in the world ocean, and their subsequent impact on particulate (DMSPp) and dissolved (DMSPd) DMSP concentrations. Under elevated pCO_2 (690 ppm) and elevated temperature (ambient + 4°C), coccolithophorid and pelagophyte abundances were significantly higher than under control conditions (390 ppm CO_2 and ambient temperature). This shift in phytoplankton community structure also resulted in an increase in DMSPp concentrations[337].

329 Wootton, T. J., Pfister, C. A., Forester, D. (2008). Dynamic patterns and ecological impacts of declining ocean pH in a high-resolution multi-year dataset. PNAS, Vol. 105(48): 18848–18853.

330 The Royal Society (2005). Ocean Acidification due to increasing atmospheric carbon dioxide. Policy Document 12/05. http://royalsociety.org/document.asp?id=3249

331 OSPAR Commission (2006). Effects of the marine environment of ocean acidification resulting from elevated levels of CO_2 in the atmosphere.

332 Kite-Powell, H. L. (2009). A Global Perspective on the Economics of Ocean Acidification. The Journal of Marine Education, Vol 25 (1):25 – 29.

333 The Royal Society (2005). Ocean Acidification due to increasing atmospheric carbon dioxide. Policy Document 12/05. http://royalsociety.org/document.asp?id=3249

334 Levasseur, M., Scarratt, M. G., Michaud, S., *et al.* (2006). DMSP and DMS dynamics during a mesoscale iron fertilization experiment in the Northeast Pacific – Part 1: Termporal and vertical distributions. Deep-Sea Research II 53, 2353–2369.

335 Fuhrman, J. A. (1991). Possible biogeochemical consequences of ocean fertilization. Limnol. Oceanogr., 36(8), 1951–1959.

336 The Royal Society (2005). Ocean Acidification due to increasing atmospheric carbon dioxide. Policy Document 12/05. http://royalsociety.org/document.asp?id=3249

337 Lee, P. A., Rudisill, J. R., Neeley, A. R., Maucher, J. M., Hutchins, D. A., Feng, Y., Hare, C. E., Leblanc, K., Rose, J. M., Wilhelm, S. W., Rowe, J. M., DiTullio, G. R., 2009. Effects of increased pCO_2 and temperature on the North Atlantic spring bloom. III. Dimethylsulfoniopropionate. *Marine Ecology Progress Series*, 388: 41–49

F. IMPACTS ON ECOSYSTEM SERVICES AND LIVELIHOODS

The oceans provide numerous ecosystem services that benefit humankind. These services, such as fisheries, contribute significantly to global employment and economic activity. Other services provided by the oceans, for example providing a site for the release of wastes and pollutants, are less well accounted for by standard economic measures. Attempts to quantify some of these services have produced estimates of many billions of dollars[338]. In contrast to the terrestrial biosphere, marine ecosystems have evolved in a comparatively homogenous environment under relatively stable conditions and over evolutionary timescales. Therefore, even subtle changes in the environmental conditions may have strong effects on ecosystem functioning, with yet unforeseen consequences for the continued provision of key services. Furthermore, marine ecosystems are likely to become less robust as a result of the projected changes to ocean chemistry and more vulnerable to other environmental impacts, such as large-scale fishing and increasing sea-surface temperatures.

Tropical coral reefs provide ecosystem services that are vital to human societies and industries, including building materials and reef-based tourism (direct use values); habitat and nursery functions for commercial and recreational fisheries, and coastal protection (indirect use values); and the welfare associated with the existence of diverse natural ecosystems (preservation values)[339]. Coral reefs produce 10–12% of the fish caught in the tropics and 20–25% of the fish caught by developing nations[340]. Many developing countries have tourism as their primary income earner and are at risk if their coral reefs deteriorate. For example, reef-based tourism is a major foreign exchange earner in the Caribbean basin, accounting for many billions of US$ per year from visitors who are increasingly responsive to the quality of the natural environment[341].

Reefs in acidified waters are predicted to decline in the following sequence: (a) loss of coralline algae causing decreased reef consolidation; (b) loss of carbonate production by corals resulting in loss of habitat; (c) loss of biodiversity with extinctions. The failure of coral communities to compete with algae communities that will not be similarly affected by ocean acidification will result in an ecological phase shift to a stable new ecosystem state dominated by less commercially valuable species[342]. The annual economic damage of ocean acidification-induced coral reef loss is estimated to rapidly escalate over time due to economic growth, reaching US$ 870 billion by 2100, under the A1 SRES global emissions scenario[343].

Overall impacts on ecosystem services will be a result of synergistic effects of several pressures in co-action, such as ocean exploitation and pollution[344]. It is anticipated that decreasing rates of reef accretion, increasing rates of bio-erosion, rising sea levels, and intensifying storms due to future climate change influences may combine to jeopardize the coastal protection function of coral reefs. People, infrastructure, and lagoon and estuarine ecosystems, including mangroves, seagrass meadows, and salt marshes,

338 The Royal Society (2005). Ocean Acidification due to increasing atmospheric carbon dioxide. Policy Document 12/05. http://royalsociety.org/document.asp?id=3249

339 Moberg, Fredrik and Folke, Carl (1999). Ecological goods and services of coral reef ecosystems. Ecological Economics 29, 215–233.

340 Garcia, S. M., Moreno, D. (2001). Global overview of marine fisheries. Report of the conference on Responsible Fisheries in the Marine Ecosystem. (ftp://ftp.fao.org/fi/DOCUMENT/reykjavik/Default.htm), Reykjavik, Iceland, 1–4 October 2001.

341 Hoegh-Guldberg, O., Mumby, P. J., Hooten, A. J., Steneck, R. S., Greenfield, P., Gomez, E., Harvell, C. D., Sale, P. F., Edwards, A. J., Caldeira, K., Knowlton, N., Eakin, C. M., Iglesias-Prieto, R., Muthiga, N., Bradbury, R. H., Dubi, A., and Hatziolos, M. E. (2007). Coral reefs under rapid climate change and ocean acidification. *Science* 318, 1737–1742.

342 Veron, J. E. N. 2009. The future of the Great Barrier Reef: highlighting the global threat to coral reefs. Briefing notes for the Royal Society Workshop July 6 2009.

343 Brander, L. M., Rehdanz, K., Tol, R. S. J., and van Beukering, P. J. H. (2009). The Economic Impact of Ocean Acidification on Coral Reefs. *Working Paper No. 282 . ESRI*: Dublin, Ireland.

344 Jackson, J. B. C. (2008). Ecological extinction and evolution in the brave new ocean. *Proceedings of the National Academy of Sciences of the United States of America* 105, 11458–11465.

will become increasingly vulnerable to growing wave and storm impacts[345]. These changes could fundamentally alter the nature of coastlines and the resources available to human societies that depend on them. A more thorough understanding of the specific impacts of ocean acidification is urgently needed in the face of the importance of the ocean's ecosystem services to aid planning and informed responses to the emerging challenges[346].

Ocean acidification will slow or reverse marine plant and animal carbonate shell and skeleton growth, with a corresponding decrease in fishing revenues with significant impacts for communities that depend on the resources for income and livelihoods[347]. The economic consequences will depend on the combined adaptation of marine ecosystems and human resource management efforts. In 2006, shellfish and crustaceans provided 50% of the US$ 4 billion domestic commercial harvest value in the USA. Processing, wholesale, and retail activities led to sales of US$ 69.5 billion, contributing US$ 35 billion in value added to the U.S gross national product, and providing an estimated 70,000 jobs[348]. Ocean acidification-driven declines in commercial shellfish and crustacean harvests from present day to 2060 could decrease U.S. primary commercial revenues by US$ 860 million to US$ 14 billion, depending on CO_2 emissions, discount rates, biological responses and fishery structure. This estimate excludes losses from coral reef damage and possible fishery collapses if ocean acidification pushes ecosystems past ecological tipping points[349].

Economic changes resulting from fishery losses on a local scale could alter the dominant economic activities and demographics, and accelerate the proportion of the population living below the poverty line in dependent communities that have little economic resilience or few alternatives[350]. For example, coastal and marine related industries comprise approximately 25% of Indonesia's gross domestic product and employ nearly 15% of that country's workforce[351].

The total value of world fisheries production is presently around US$ 150 billion per year. Approximately 50% of all food fish comes from aquaculture industries, which depend heavily on carbonate-forming organisms like shellfish and crustaceans as a source of broodstock for hatcheries[352]. Most aquaculture facilities are located in coastal areas, which will likely experience ocean acidification[353]. Reduced calcification and reproduction success in calcifying organisms will represent a significant loss of economic and livelihood opportunities from aquaculture and commercial fisheries sectors, and are likely to affect developing countries that are more reliant on aquaculture sources for the provision of protein and revenue. While hard to predict, early estimates of the direct impacts of ocean acidification on marine fishery production are in the order of US$ 10 billion per year[354].

345 Hoegh-Guldberg, O., Mumby, P. J., Hooten, A. J., Steneck, R. S., Greenfield, P., Gomez, E., Harvell, C. D., Sale, P. F., Edwards, A. J., Caldeira, K., Knowlton, N., Eakin, C. M., Iglesias-Prieto, R., Muthiga, N., Bradbury, R. H., Dubi, A., and Hatziolos, M. E. (2007). Coral reefs under rapid climate change and ocean acidification. *Science* 318, 1737–1742.

346 IPCC (2007) Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change. Cambridge University Press: Cambridge, UK and New York, NY, USA

347 Kleypas, J. A., Feely, R. A., Fabry, V. J., Langdon, C., Sabine, C. L., Robbins, L. L. (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 U.S Geological Survey, 88 pp.

348 Cooley, S. R., Doney, S. C. (2009). Ocean Acidification's impact on Fisheries and Societies: A U.S Perspective. *Journal of Marine Education*, 25(1):15–19.

349 Cooley, S. R., Doney, S. C. (2009). Economic vulnerability assessment of U.S. fishery revenues to ocean acidification. Submitted to Proceedings of the National Academy of Sciences of the United States of America. www.pnas.org/cgi/doi/10.1073/pnas.0709640104.

350 Cooley, S. R., Doney, S. C. (2009). Ocean Acidification's impact on Fisheries and Societies: A U.S Perspective. *Journal of Marine Education*, 25(1):15–19.

351 Kite-Powell, H. L. (2009). A Global Perspective on the Economics of Ocean Acidification. *Journal of Marine Education*, Vol 25 (1):25 – 29.

352 Ibid.

353 Cooley, S. R., Doney, S. C. (2009). Ocean Acidification's impact on Fisheries and Societies: A U.S Perspective. *Journal of Marine Education*, 25(1):15–19.

354 Kite-Powell, H. L. (2009). A Global Perspective on the Economics of Ocean Acidification. *Journal of Marine Education*, Vol 25 (1):25 – 29.

IV. UNCERTAINTIES AND OTHER CONSIDERATIONS

How is calcification affected in organisms at different stages of their life cycle?

Marine organisms use ions in seawater to form a variety of shells, exoskeletons, and internal structures made of carbonate minerals. Structures can contain several minerals, non-mineral layers, or both, and the minerals used can vary by organisms' developmental stage. Different life cycle stages of benthic calcifiers display different morphologies and modes of calcification, which can influence the response of the organism to changes in CO_2 concentration and pH[355]. Larval and juvenile stages may be particularly sensitive, in part because they form their internal skeletons out of amorphous calcite, which is more soluble that other forms of carbonate[356]. Low pH can cause decreased $CaCO_3$ skeleton assimilation, and a corresponding decrease in the length of free swimming pluteus larvae in phytoplankton and coral. A reduction in protein synthesis is observed following fertilization of sea urchin *Hemicentrotus pulcherrimus,* which leads to decreased growth and cleavage rates[357]. Any delay in the developmental rate of organisms increases the mortality of embryos during the planktonic period due to predation. The morphology of pluteus larvae grown at pH 6.8 was observed to be extremely abnormal, lacking arms, which have an important function for swimming and feeding, and therefore survival rates. Fertilization rates, reproduction, fertilization, planktonic larva, settlement, metamorphosis, and juvenile and benthic adult stages, are potentially affected in different ways by ocean acidification (Figure 16).

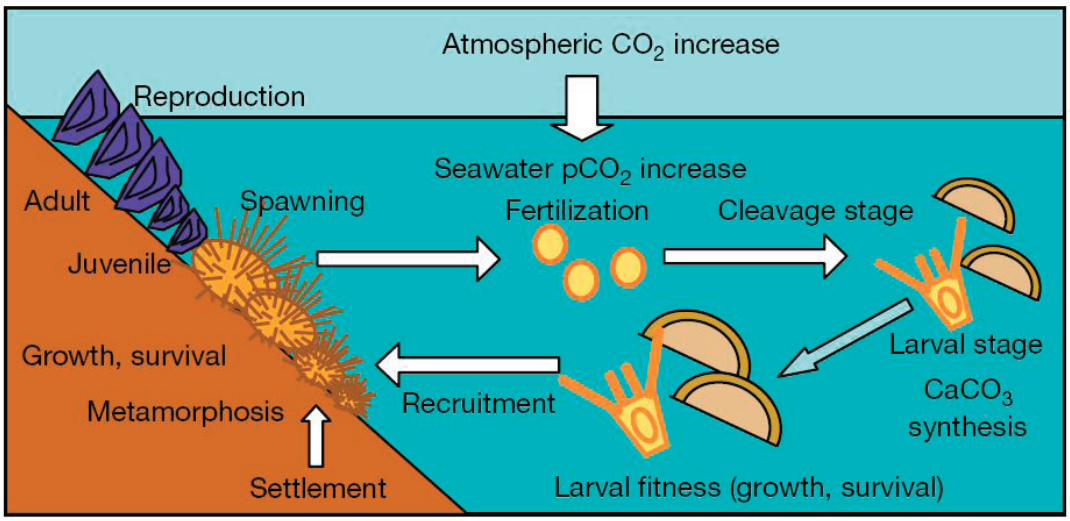


FIGURE 16: Effects of CO_2-driven ocean acidification on the early development stages of invertebrates. *Source: Kurihara, H. (2008)*[358].

355 Rost, B., Zondervan, I., Wolf-Gladrow, D. (200*) Sensitivity of phytoplankton to future changes in ocean carbonate chemistry: current knowledge, contradictions and research directions. *Mar Ecol Prog Ser*, Vol. 373:227–237.

356 Vezina, A. F., Hoegh-Guldberg, O. (2008). Introduction to: Effects of ocean acidification on marine ecosystems. *Mar Ecol Prog Se*, Vol 373:199–201.

357 Kurihara, H., Shirayama, Y. (2004). Effects of increased atmospheric CO_2 on sea urchin early development. *Mar Ecol Prog Ser*. 274:161–169.

358 Kurihara, H. (2008). Effects of CO_2 driven ocean acidification on the early developmental stages of invertebrates. *Mar Ecol Prog Ser*. 373:275–284.

Why do some calcifying organisms seem to be less affected than others?

Contrary to expectation, elevated pCO_2 levels have been reported to enhance structural calcification in species of coccolithophores, some invertebrates, e.g. juvenile cephalopod mollusc[359], and juvenile fish[360]. This follows recent suggestions that the biological responses to ocean acidification, especially in calcifying biota, will be species-specific and therefore much more variable and complex than previously reported[361].

To alleviate the risk of carbon limitation, many marine phytoplankton are thought to have developed physiological mechanisms to actively concentrate CO_2 in their cells so that changes in seawater pH and CO_2 have little if any direct effect on their growth rate or their elemental composition. Taxon-specific differences in CO_2 sensitivity have been observed in laboratory culture but it is currently unknown whether energetic demands of this compensatory mechanism will impact phytoplankton species diversity, or the contribution of different functional groups in the natural environment[362]. In general, species relying on diffusive CO_2 uptake or those with inefficient CO_2-concentrating mechanisms (CCM) are highly CO_2 sensitive in photosynthesis and may benefit from the increase in CO_2 in future oceans. Those species operating highly efficient CCMs are at rate saturation under present-day CO_2 concentrations. However, a down regulation of the CCM under elevated CO_2 levels may allow for optimized energy and resource allocation in these species[363]. CCMs are thought to be less widespread in benthic photosynthetic organisms[364].

Some experiments have shown both increasing[365] and decreasing[366] coccolithophore calcification under elevated CO_2 conditions, even in the same species. These conflicting results may be caused by genetic differences between the strains used, or differences in laboratory and experimental procedures, highlighting the need for standardised methods and protocols, and accurate interpretations of the available data[367].

How is adaptation and survival influenced by the different mechanisms of calcification or other physiological factors?

The high rate of increase in CO_2 concentration means that organisms are being exposed to changes that are faster than they have encountered in their recent evolutionary history[368]. The capacity of calcifying marine organisms to adapt to progressively acidified oceans is not known, but may be a function of species generation time, which suggests that long-lived species, such as warm- and cold-water corals,

359 Gutowska M., A., Pörtner H.-O., Melzner F., (2008). Growth and calcification in the cephalopod *Sepia officinalis* under elevated seawater pCO_2. *Marine Ecology Progress Series* 373:303–309.

360 Checkley Jr., D. M., Dickson, A. G., Takahashi, M., Radich, J. A., Eisenkolb, N., Asch, R. (2009). Elevated CO_2 enhances otolith growth in young fish. *Science* 324: 1683.

361 Miller, A. W., Reynolds, A. C., Sobrino, C., Reidel, G. F. (2009). Shellfish Face Uncertain Future in High CO_2 World: Influence of Acidification on Oyster Larvae Calcification and Growth in Estuaries. *PLOSOne*, 4(5) e5561.

362 OSPAR Commission (2006). Effects of the marine environment of ocean acidification resulting from elevated levels of CO_2 in the atmosphere.

363 Rost, B., Zondervan, I., Wolf-Gladrow, D. (200*) Sensitivity of phytoplankton to future changes in ocean carbonate chemistry: current knowledge, contradictions and research directions. Mar Ecol Prog Ser, Vol. 373:227–237.

364 The Royal Society (2005). Ocean Acidification due to increasing atmospheric carbon dioxide. Policy Document 12/05. http://royalsociety.org/document.asp?id=3249

365 Iglesias-Rodriguez, M. D., Halloran, P. R., Rickaby, R. E. M., Hall, I. R., Colmenero-Hidalgo, E., Gittins, J. R., Green, D. R. H., Tyrell, T., Gibbs, S. J., von Dassow, P., Rehm, E., Armbrust, E. V., Boessenkool, K. P. (2008). Phytoplankton Calcification in a High-CO_2 World. Science, 320:336–340.

366 Wolf-Gladrow, D. A., Riebesell, U., Burkhardt, S., Bjima, J. (1999). Direct effects of CO_2 concentration on growth and isotopic composition of marine plankton. Tellus 51B:461–476.

367 Reibesell, U., Bellerby, R. G. J., Engel, A., Fabry, A., Hutchins, D. A., Reusch, T. B. H., Schulz, K. G., Morel, F. M. M. (2008) Comment on "Phytoplankton Calcification in a High-CO_2 World". Science, 322 (5907):1466.

368 The Royal Society (2005). Ocean Acidification due to increasing atmospheric carbon dioxide. Policy Document 12/05. http://royalsociety.org/document.asp?id=3249

will be less able to respond. Shorter generation times may afford increased opportunities for micro-evolutionary adaptation[369].

Commercially valuable molluscs, such as bivalves and some gastropods, exert low biological control over the calcification process and depend on specific ambient seawater chemistry that promotes $CaCO_3$ deposition. Sea urchins and crustaceans, including lobsters and shrimp, exert higher biological control by gradually accumulating intracellular stocks of ions; between moults, crustaceans are thought to harden their chitin and protein exoskeletons by continually depositing calcite minerals. The shell chemistry and mineralization of crustaceans suggest that they may withstand ocean acidification and saturation state decreases better than molluscs, however the response of organisms is likely to be a function of individual history and genetic variability[370].

Owing to their highly soluble aragonitic shells and high population densities in polar and sub-polar waters, which will be the first regions of the oceans to experience under-saturation with regards to aragonite, pteropods may be particularly sensitive to ocean acidification. It is likely that given the rate of change, pteropods will not be able to adapt quickly enough to live in the under-saturated conditions that will occur over much of the high-latitude surface ocean during the 21st century. Their distributional ranges will be reduced both within the water column, disrupting vertical migration patterns, and latitudinally, imposing a shift towards lower latitude surface waters that remain supersaturated with respect to aragonite[371]. Few experiments have been conducted for long enough to indicate whether organisms will be able to genetically adapt to these changes.

How do other environmental factors such as carbonate concentration, light levels, temperature and nutrients affect calcification processes?

Substances other than the components of the carbonate system are important for supporting life in the oceans, such as macro- and micro-nutrients and trace elements. Ocean acidification is expected to produce changes in ocean chemistry that may affect the availability of nutrients and the toxicity and speciation of trace elements to marine organisms, however the extent of the pH-induced changes are difficult to determine. Variation in the availability of nutrients may have an indirect effect on cellular acquisition, the growth of photosynthetic organisms, or the nutritional value of micro-organisms to higher orders of the food chain[372]. Additionally, non-photosynthetic micro organisms, such as bacteria, fungi and protists, may benefit from increased CO_2 concentrations and altered speciation.

The pH of the oceans fluctuates with available sunlight, increasing phytoplankton abundance, upwelling, alkalinity, and water temperature, indicating that biological processes influence ocean pH. Indeed, the ionisation of nutrients supplied as solutes, and critical for phytoplankton nutrition, varies across a range of pH values[373]. It is important therefore that future models and experiments of ocean pH capture the influence of these other variables on calcification processes, which have not always been accounted for in previous work[374].

369 Ibid.

370 Cooley, S. R., Doney, S. C. (2009??). Economic vulnerability assessment of U.S. fishery revenues to ocean acidification. Submitted to Proceedings of the National Academy of Sciences of the United States of America. www.pnas.org/cgi/doi/10.1073/pnas.0709640104.

371 Orr, J. C., Fabry, V. J., Aumont, O., Bopp, L., Doney, S. C., *et al.* (2005). Anthropogenic ocean acidification over the twenty-first century and its impact on calcifying organisms. Nature 437:681–686.

372 The Royal Society (2005). Ocean Acidification due to increasing atmospheric carbon dioxide. Policy Document 12/05. http://royalsociety.org/document.asp?id=3249

373 Ibid.

374 Kleypas, J. A., Feely, R. A., Fabry, V. J., Langdon, C., Sabine, C. L., Robbins, L. L. (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 U.S Geological Survey, 88 pp.

How will communities with a mixture of calcifying and non-calcifying organisms respond to decreased calcification rates, and what impact will this have on the marine food chain?

The complex and non-linear effects of ocean acidification, and the limited available data on the change in relative abundance of species as CO_2 increases in the oceans, makes the accurate prediction of community responses challenging. Observations from naturally acidified marine environments, such as Ischia in Italy, reveal that low pH causes major ecological shifts, dramatically impacting the surrounding biological communities, and provides invaluable information about the ecosystem-level impacts of ocean acidification[375].

In Ischia waters with a mean pH of 7.8, the number of species is 30% lower than at sites with a normal pH. Organisms with calcareous structures (e.g. epiphytic worms commonly found on sea-grass leafs), or shells (snails, mussels, sea urchins, barnacles) are absent or severely reduced in low pH areas. Furthermore, the abundance of sea urchins, the most common large invertebrates on sub-littoral rock outside the vents, is significantly reduced where pH reaches minima of 7.4–7.5 units. Instead, areas close to CO_2 vents are covered by lush sea-grass meadows and algal communities, which use dissolved CO_2 directly, and thrive in or are resilient to, high CO_2 concentrations[376].

The net effect of increasing CO_2 on sea grass ecosystems will be increased sea grass biomass and productivity. It is probable that an increase in total sea grass area will lead to more favourable habitat and conditions for associated invertebrate species and fish species. However, the net effect of ocean acidification on coral reef ecosystems will be negative as many warm-water corals will be heavily impacted by the combined effects of increasing sea surface temperatures and decreasing carbonate saturation states of surface waters in the coming decades.

375 Hall Spencer, J., Rauer, E. (2009). Champagne Seas – Fortelling the Ocean's Future? *Current: The Journal of Marine Education*, Vol. 25(1):11–12

376 Hall-Spencer, J. M., Rodolfo-Metalpa, R., Martin, S., Ransome, E., Fine, M., Turner, S. M., Rowley, S. J., Tedesco, D., Buia, M. C. (2008). Volcanic carbon dioxide vents show ecosystem effects of ocean acidification. *Nature* 454:96–99.

V. CONCLUSIONS

The global atmospheric concentration of CO_2 has increased from a pre-industrial value of 280 ppm to 384 ppm[377], leading to a 30% increase in the acidity of the oceans. This significant increase is 100 times faster than any change in acidity experienced in the marine environment for the last 20 million years and represents a rare geological event in the Earth's history[378, 379].

Atmospheric CO_2 concentrations are predicted to increase throughout the 21st century and could exceed 800 ppm by 2100 if anthropogenic emissions continue along current trends[380]. Ocean acidification is a direct consequence of increasing atmospheric CO_2 concentrations that is occurring independently of climate change. It can be predicted with a high level of certainty based on the complex but predictable marine carbonate chemistry reactions and cycles of CO_2 as it dissolves in seawater. Ocean acidification will follow the accelerating trend in world CO_2 emissions, leading to a 150–185% increase in acidity by 2100, under current emission rates (a decrease of 0.4–0.45 pH units)[381].

Increasing ocean acidification reduces the availability of carbonate minerals (aragonite and calcite) in seawater, important building blocks for marine plants and animals. Carbonate ion concentrations are now lower than at any other time during the last 800,000 years[382]. Experimental evidence has demonstrated that increased pCO_2 (560ppm) has a negative effect on calcification, causing a decrease in calcification rates of between 5–60% in corals, coccolithophores, and foraminifera[383, 384, 385]. As the world's oceans become less saturated with carbonate minerals over time, marine organisms are expected to build weaker skeletons and shells, and experience slower growth rates which will make it increasingly difficult to retain a competitive advantage over other marine organisms.

The $CaCO_3$ saturation horizon above which $CaCO_3$ can form, and below which it readily dissolves, has shoaled significantly in certain parts of the ocean, by up to 150 m in the Atlantic, reducing the available habitat for important calcifying organisms[386]. As seawater becomes under-saturated with respect to these minerals it becomes corrosive, and the shells of calcifying organisms are increasingly prone to dissolution. Indeed, by 2100, 70% of cold-water corals will be exposed to corrosive waters[387]. Cold-water coral reef ecosystems provide habitat, feeding grounds and nursery areas for many deep-water organisms, and support characteristic and commercially important fauna several times as diverse as that found on the surrounding seabed[388].

377 Solomon, S., Quinn, D., Manning, M., Chen, Z., Marquis, M., Averyt, K. B., Tignor, M., Miller, H. (eds) (2007). *Climate Change 2007: The Physical Science Basis*. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change. New York: Cambridge University Press.

378 Turley, C. M., Roberts, J. M., Guinotte, J. M. (2007). Corals in deepwater: will the unseen hand of ocean acidification destroy cold-water ecosystems. *Coral Reefs* 26:445–448.

379 UNESCO, IGBP, MEL, SCOR. (2009). Ocean Acidification: A Summary for Policymakers from the Second Symposium on the Ocean in a High-CO_2 World. www.ocean-acidification.net

380 Feely, R. A., Sabine, C. L., Hernandez-Ayon, J. M., Lanson, D., Hales, B. (2008). Evidence for Upwelling of Corrosive "Acidified" Water onto the Continental Shelf. *Science* 320:1490 -1492.

381 Steinacher, M., Joos, F., Frölicher, T. L., Plattner, G.-K., Doney, S. C. (2009). Imminent ocean acidification in the Arctic project with the NCAR global coupled carbon cycle-climate model. *Biogeosciences* 6:515–533.

382 Inter-Academy Panel on International Issues (IAP) (2009). Statement on Ocean Acidification. Endorsed, June 2009. www.interacademies.net/CMS/9075.aspx

383 Feely, R. A., Sabine, C. L., Lee, K., Berelson, W., Kleypas, J., Fabry, V. J., Millero, F. J. (2004). Impact of anthropogenic CO_2 on the $CaCO_3$ system in the oceans. *Science* 305:362–365.

384 Kleypas, J. A., Feely, R. A., Fabry, V. J., Langdon, C., Sabine, C. L., Robbins, L. L. (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 U.S Geological Survey, 88 pp.

385 Fine, M., Tchernov, D. (2007). Scleractinian Coral Species Survive and Recover from Decalcification. *Science* 315:1811.

386 Feely, R. A., Sabine, C. L., Lee, K., Berelson, W., Kleypas, J., Fabry, V. J., Millero, F. J. (2004). Impact of anthropogenic CO_2 on the $CaCO_3$ system in the oceans. *Science* 305:362–365.

387 Guinotte, J. M., Orr, J., Cairns, S., Freiwald, A., Morgan, L., George, R. (2006). Will human-induced changes in seawater chemistry alter the distribution of deep-sea scleractinian corals? *Front Ecol Environ* 4(3):141–146.

388 Turley, C. M., Roberts, J. M., Guinotte, J. M. (2007). Corals in deepwater: will the unseen hand of ocean acidification destroy cold-water ecosystems. *Coral Reefs* 26:445–448.

Tropical coral reefs provide in excess of US$ 30 billion annually in global goods and services, such as shoreline protection, tourism and food security[389]. The Great Barrier Reef, Coral Sea, and Caribbean Sea are predicted to experience low aragonite saturation levels more rapidly than other tropical regions as pCO_2 increases, making large areas of the oceans inhospitable to coral reefs, and impacting the continued provision of the goods and services that these reefs provide to millions of the world's poorest people[390], and will therefore have negative impacts on marine ecosystems.

Ocean acidification research is still in its infancy, and many questions remain related to its biological and biogeochemical consequences, and the accurate determination of sub-critical levels, or tipping points for global marine species, ecosystems and the services and functions provided. The impacts will depend to some extent on the specific physiological adaptation mechanisms of species, and the energetic costs of maintaining these over the long term. Future changes in ocean acidity will potentially impact the population size, dynamics as well as community structure of calcifiers in favour of those that rely less on calcium[391]; it will negatively affect shellfish; it will impact fish; it may benefit highly invasive non-native algal and invertebrate (such as tunicate) species; and it will reduce coral calcification[392]. However, while the initial impact of ocean acidification is relatively clear, the eventual impact depends on the complex interaction of many other variables. The estimation of resulting changes in economic values, which generally derive from the higher tropic levels, is therefore also pervaded by uncertainty. What is clear is that the goods and services provided by the ocean, upon which human populations are dependent, will be different under future acidified oceans as increasing pCO_2 concentrations influence the physiology, development and survival of marine organisms[393]. There is an urgent need for more spatially distributed and temporally intensive studies of ocean pH dynamics and their underlying causal mechanisms and consequences,[394] and a focus on the adaptive capacities of marine organisms, which will be crucial to forecasting how organisms and ecosystems will respond as the world's oceans warm and acidify[395].

Theory and an emerging body of research suggest that many of the effects of ocean acidification may be non-linear, and both positive and negative feedback mechanisms on marine ecosystems seem to exist, impeding the ability to make reliable predictions of the consequences of changing CO_2 levels[396]. The ocean is one of the largest natural reservoirs of carbon, absorbing ~26–29% of anthropogenic carbon emissions each year. However, the oceans' capacity to absorb atmospheric CO_2 is being degraded by ocean acidification, which will make it more difficult to stabilize atmospheric CO_2 concentrations. Even with stabilisation of atmospheric CO_2 at 450 ppm, ocean acidification will have profound impacts on many marine ecosystems. The interactive effects of saturation state, temperature, light and nutrients are all important factors in calcification rates of organisms. Human activities are causing changes in all of these factors[397].

389 Kite-Powell, H. L. (2009). A Global Perspective on the Economics of Ocean Acidification. *Journal of Marine Education* 25 (1):25 – 29.

390 OSPAR Commission (2006). Effects of the marine environment of ocean acidification resulting from elevated levels of CO_2 in the atmosphere.

391 Guinotte, J. M., Fabry, V. J. (2008). Ocean acidification and its potential effects on marine ecosystems. *Ann. N. Y. Acad. Sci.* 1134: 320.

392 Brander, L. M., Rehdanz, K., Tol, R. S. J., and van Beukering, P. J. H. (2009). The Economic Impact of Ocean Acidification on Coral Reefs. Working Paper No. 282 . ESRI: Dublin, Ireland.

393 Andersson, A. J., Mackenzie, F. T., Bates, N. R. (2008). Life of the margin: implications of ocean acidification on Mg-calcite, high latitude and cold-water marine calcifiers. *Mar Ecol Prog Ser*. 373:265–273.

394 Wootton, T. J., Pfister, C. A., Forester, D. (2008). Dynamic patterns and ecological impacts of declining ocean pH in a high-resolution multi-year dataset. PNAS, Vol. 105(48): 18848–18853.

395 Kurihara, H. (2008). Effects of CO_2 driven ocean acidification on the early developmental stages of invertebrates. *Mar Ecol Prog Ser* 373:275–284.

396 Turley, C., Blackford, J. C., Widdicombe, S., Lowe, D., Nightingale, P. D., and Rees, A. P. (2006). Reviewing the Impact of Increased Atmospheric CO_2 on Oceanic Ph and the Marine Ecosystem. In: Avoiding Dangerous Climate Change. (H. J. Schellnhuber, W. Cramer, N. Nakicenovic, T. Wigley, and G. Yohe, Eds.) Cambridge University Press: Cambridge, UK. pp. 65–70.

397 Kleypas, J. A., Feely, R. A., Fabry, V. J., Langdon, C., Sabine, C. L., Robbins, L. L. (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 U.S Geological Survey, 88 pp.

A host of pervasive stressors are impacting the oceans, such as rising ocean temperatures, over-fishing and land-based sources of pollution, which operate in synergy with increasing acidification to compromise the health and continued function of many marine organisms. If pushed far enough, ecosystems may exceed a tipping point" and change rapidly into an alternative state with reduced biodiversity, value and function[398]. The cumulative impacts or interactive effects of multiple stressors will have more significant consequences for biota that any single stressor[399]. When considered in the light of global climate change and increasing thermal anomalies, coral reef acidification and bleaching enhance deleterious ecosystem feedbacks, driving the coral ecosystems toward domination by macroalgae and non-coral communities[400].

Ocean acidification is irreversible on short-term timeframes, and substantial damage to ocean ecosystems can only be avoided through urgent and rapid reductions in global emissions of CO_2 by at least 50% by 2050, and much more thereafter[401]. Ocean acidification is an already observable and predictable consequence of increasing atmospheric CO_2 concentrations, with biological impacts, and will need to be recognized and integrated into the global climate change debate.

398 Hoegh-Guldberg, O., Mumby, P. J., Hooten, A. J., Steneck, R. S., Greenfield, P., Gomez, E., Harvell, C. D., Sale, P. F., Edwards, A. J., Caldeira, K., Knowlton, N., Eakin, C. M., Iglesias-Prieto, R., Muthiga, N., Bradbury, R. H., Dubi, A., and Hatziolos, M. E. (2007). Coral reefs under rapid climate change and ocean acidification. Science 318, 1737–1742.

399 Guinotte, J. M., Fabry, V. J. (2008). Ocean acidification and its potential effects on marine ecosystems. Ann. N. Y. Acad. Sci. 1134: 320.

400 Hoegh-Guldberg, O., Mumby, P. J., Hooten, A. J., Steneck, R. S., Greenfield, P., Gomez, E., Harvell, C. D., Sale, P. F., Edwards, A. J., Caldeira, K., Knowlton, N., Eakin, C. M., Iglesias-Prieto, R., Muthiga, N., Bradbury, R. H., Dubi, A., and Hatziolos, M. E. (2007). Coral reefs under rapid climate change and ocean acidification. Science 318, 1737–1742.

401 Inter-Academy Panel on International Issues (IAP). 2009. Statement on Ocean Acidification. Endorsed, June 2009. www.interacademies.net/CMS/9075.aspx