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AN UPDATED SYNTHESIS OF THE IMPACTS OF OCEAN ACIDIFICATION ON MARINE BIODIVERSITY

Note by the Executive Secretary

1. In decision XI/18, the Conference of the Parties to the Convention on Biological Diversity requested the Executive Secretary to collaborate with the Intergovernmental Oceanographic Commission of the United Nations Educational, Scientific and Cultural Organization, relevant scientific groups, other relevant organizations, and indigenous and local communities on the preparation of a systematic review document on the impacts of ocean acidification on biodiversity and ecosystem functions, which will provide a targeted synthesis of the biodiversity implications of ocean acidification for marine and coastal systems, including information on the less-reported paleo-oceanographic research, building upon the synthesis provided in CBD Technical Series No. 46.

2. Pursuant to the above request, the Secretariat has prepared an updated synthesis of the impacts of ocean acidification on marine biodiversity. This document was developed through scientific compilation, coordination and synthesis work kindly supported by the United Kingdom of Great Britain and Northern Ireland in collaboration with a team of international experts. The first draft was circulated for peer-review by Parties, other Governments and relevant organizations (notification 2014-004, Ref. No SCBD/SAM/DC/JL/JM/83041, issued on 10 January 2014).

3. The revised draft, which incorporated the comments and suggestions from the peer-review, is being submitted for consideration to the Subsidiary Body at its eighteenth meeting.

** Reposted on 19 June 2014 for technical reasons.

* UNEP/CBD/SBSTTA/18/1.

An updated synthesis of the impacts of ocean acidification on marine biodiversity

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Organizations: Intergovernmental Oceanographic Commission of the UN Educational, Scientific and Cultural Organisation; International Atomic Energy Agency; UN Division for Ocean Affairs and the Law of the Sea.

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EXECUTIVE SUMMARY

Ocean acidification and awareness of its consequences

1. **Ocean acidification has increased by around 30% since pre-industrial times**
   In the past 200 years, it is estimated that the ocean has absorbed more than a quarter of the carbon dioxide released by human activity, increasing ocean acidity (hydrogen ion concentration) by a similar proportion. It is now near-inevitable that within 50-100 years, continued anthropogenic carbon dioxide emissions will further increase ocean acidity to levels that will have widespread impacts, mostly deleterious, on marine organisms and ecosystems, and the goods and services they provide. Marine calcifying organisms seem particularly at risk, since additional energy will be required to form shells and skeletons, and in many ocean areas, unprotected shells and skeletons will dissolve.

2. **International awareness of ocean acidification and its potential consequences is increasing**
   Many programmes and projects are now investigating the impacts of ocean acidification on marine biodiversity and its wider implications, with strong international linkages. The UN General Assembly has urged States to study ocean acidification, minimise its impacts and tackle its causes. Many UN bodies are giving attention to these issues.

Global status and future trends of ocean acidification

3. **Seawater pH shows substantial natural temporal and spatial variability**
   The acidity of seawater varies naturally on a diurnal and seasonal basis, on a local and regional scale, and as a function of water depth. Coastal ecosystems and habitats experience greater variability than those in the open ocean, due to physical, geochemical and biological processes, and terrestrial influences.

4. **Substantial natural biological variability exists in organisms' responses to pH changes**
   Metadata analyses, combining results from many experimental studies, show that there are different, but consistent, patterns in the response of different taxonomic groups to simulated future ocean acidification. There can also be variability in responses within species, depending on interactions with other factors.

5. **Surface waters in polar seas and upwelling regions are increasingly at risk of becoming unsaturated with respect to calcium carbonate, dissolving unprotected shells and skeletons**
   In waters where pH is already naturally low (in high latitudes, coastal upwelling regions and on the shelf slope) widespread undersaturation of both aragonite and calcite is expected to develop during this century. Benthic and planktonic molluscs are amongst the groups likely to be affected, also coldwater corals and the structural integrity of their habitats.

6. **International collaboration is underway to improve ocean acidification monitoring, closely linked to other global ocean observing systems**
   A well-integrated global monitoring network for ocean acidification is crucial to improve understanding of current variability and to develop models that provide projections of future conditions. Emerging technologies and sensor development increase the efficiency of this evolving network.

What the past can tell us: paleo-oceanographic research

7. **During natural ocean acidification events which occurred in the geological past, many marine calcifying organisms became extinct**
   High atmospheric carbon dioxide has caused natural ocean acidification in the past, linked to 'coral reef crises'. During the Paleo-Eocene Thermal Maximum (PETM, ~56 million years ago), more limited species extinctions occurred; however, the changes that occurred then were much slower than those happening today.

8. **Recovery from a major decrease in ocean pH takes many thousands of years**
The paleo-record shows that recovery from ocean acidification can be extremely slow; for example, around 100,000 years following the PETM.

Impacts of ocean acidification on physiological responses

9. **Ocean acidification has implications for acid-base regulation and metabolism for many marine organisms**
When external hydrogen ion levels substantially increase, extra energy may be required to maintain the internal acid-base balance. This can lead to reduced protein synthesis and reduction in fitness. Such effects are greatest for sedentary animals, but can be mitigated if food supply is abundant, and increasing metabolism may offset detrimental affects in some species.

10. **Impacts of ocean acidification upon invertebrate fertilization success are highly variable, indicating the potential for genetic adaptation**
Experimental studies on the effect of ocean acidification on fertilization show that some species are highly sensitive, whilst others are tolerant. Intra-specific variability indicates the scope for a multi-generational, evolutionary response.

11. **Ocean acidification is potentially detrimental for calcifying larvae**
Early life stages of a number of organisms seem to be particularly at risk from ocean acidification, with impacts including decreased larval size, reduced morphological complexity, and decreased calcification.

12. **Ocean acidification can alter sensory systems and behaviour in fish and some invertebrates**
Impacts include the loss of ability to discriminate between important chemical cues. Individuals may become more active, liable to exhibit bolder and more risky behaviour.

Impacts of ocean acidification on benthic communities

13. **Around half of benthic species have lower growth rates and survival under projected future acidification**
For corals, molluscs and echinoderms, many studies show reduction in growth and reduced survival with ocean acidification. However, these responses are variable, and some species can live at low pH conditions.

14. **Many seaweed (macroalgae) and seagrass species can tolerate, or may benefit from, future ocean acidification**
Non-calcifying photosynthetic species may benefit from future ocean acidification; they are frequently abundant near natural CO_2 seeps. Calcifying macroalgae are, however, negatively impacted. High densities of seagrass and fleshy macroalgae can significantly alter the local carbonate chemistry, with potential benefit for neighbouring ecosystems.

Impacts of ocean acidification on pelagic communities

15. **Many phytoplankton could potentially benefit from future ocean acidification**
Non-calcifying phytoplankton (e.g. diatoms) can show increased photosynthesis and growth under high CO_2 conditions. The response of calcifying phytoplankton (e.g. coccolithophores) is more variable, both between and within species. Mesocosm experiments provide insights into the community shifts that might arise through competitive interactions, as well as the balance between increased photosynthesis and decreased calcification. The response of bacterio-plankton to ocean acidification has not been well studied, but altered decomposition rates would have implications for nutrient cycling.

16. **Planktonic foraminifera and pteropods seem likely to experience decreased calcification or dissolution under projected future conditions**

The shells of both of these groups are liable to experience dissolution if calcium carbonate saturation drops below 1. Decreases in shell thickness and size of planktonic foraminifera may also decrease the efficiency of future carbon transport between the sea surface and the ocean interior.

Impacts of ocean acidification on biogeochemistry

17. **Ocean acidification could alter many other aspects of ocean biogeochemistry, with feedbacks to climatic processes**
High CO_2 may alter net primary productivity, trace gas emissions, nitrogen-carbon ratios in food webs and exported particulate matter, and iron bioavailability. The scale and importance of these effects are not yet well-understood.

Impacts of ocean acidification on ecosystem services and livelihoods

18. **Impacts of ocean acidification upon ecosystem services may already be underway**
Ocean acidification is apparently already impacting aquaculture in the Pacific Northwest, further decreasing the pH of upwelled water that has a naturally low saturation state for calcium carbonate. High mortalities in oyster hatcheries can, however, be mitigated by monitoring and management measures. Risks to tropical coral reefs are also of great concern, since the livelihoods of around 400 million people depend on such habitats. Research on the socio-economic impacts of ocean acidification has only recently started, and is growing rapidly.

Resolving uncertainties

19. **Existing variability in organism response to ocean acidification needs to be investigated further, to assess the potential for evolutionary adaptation**
Multi-generational studies with calcifying and non-calcifying algal cultures show that adaptation to high CO_2 is possible for some species. Such studies are more difficult for long-lived organisms, and variability in adaptive capacity is likely. Even with adaptation, community composition and ecosystem function are still likely to change.

20. **Research on ocean acidification increasingly needs to involve other stressors, as will occur under field conditions in the future**
Acidification may interact with many other changes in the marine environment, local and global; these ‘multiple stressors’ include including temperature, nutrients, and oxygen. *In situ* experiments on whole communities (using natural CO_2 vents or CO_2 enrichment mesocosms) provide a good opportunity to investigate impacts of multiple stressors on communities, to increase our understanding of future impacts.

Synthesis

21. **Ocean acidification represents a serious threat to marine bioversity, yet many gaps remain in our understanding of the complex processes involved, and their societal consequences**
Ocean acidification is currently occurring at a geologically-unprecedented rate, subjecting marine organisms to an additional, and worsening, environmental stress. Experimental studies show the variability of organisms’ responses to simulated future conditions: some are impacted negatively, some positively, and others are apparently unaffected. Furthermore, responses to ocean acidification can interact with other stressors, and vary over time, with some potential for genetic adaptation. This complexity of natural processes make it extremely challenging to assess how future ocean acidification will affect natural marine communities, food webs and ecosystems, and the goods and services they provide. Nevertheless, substantive environmental perturbations, increased extinction risk for particularly vulnerable species, and significant socio-economic consequences all seem highly likely. Research priorities to reduce the uncertainties relating to future impacts include greater use of natural high-CO_2 analogues, the geological record, and well-integrated observations, together with large-scale, longterm and multi-factorial experimental studies.

1. BACKGROUND AND INTRODUCTION

Ocean acidification, often referred to as the "other CO_2 problem" [1], is a direct result of rising atmospheric carbon dioxide (CO_2) concentrations due to the burning of fossil fuels, deforestation, cement production and other human activities. As atmospheric CO_2 increases, more enters the ocean across the sea surface. This process has significant societal benefits: by absorbing around 25% of the total human production of CO_2, the ocean has substantively slowed climate change. But it also has less desirable consequences, since the dissolved CO_2 affects seawater chemistry, with a succession of potentially adverse impacts on marine biodiversity, ecosystem services and human society.

The starting point for such changes is an increase in seawater acidity, resulting from the release of hydrogen ions (H^+). Acidity is measured on the logarithmic pH scale, with H^+ concentrations* at pH 7.0 being ten times greater than at pH 8.0. Since pre-industrial times, the mean pH in the surface ocean has dropped by 0.1 units, a linear-scale increase in acidity of ~26%. Unless CO_2 emissions are rapidly curtailed, mean surface pH is projected – with a high degree of certainty – to fall by a further ~0.3 units by 2100 [2-4]. The actual change will depend on future CO_2 emissions, with both regional and local variations (Chapter 3).

Key Messages: Chapter 1

1. Ocean acidification is a process caused by increasing levels of carbon dioxide in the atmosphere and seawater, with potentially deleterious consequences for marine species and ecosystems

2. The acidity of the surface ocean has increased by ~26% since pre-industrial levels

3. The increased international attention given to ocean acidification, by the CBD and other bodies, has catalysed research and helped identify knowledge gaps

Very many scientific studies in the past decade have unequivocally shown that a wide range of marine organisms are sensitive to pH changes of such magnitude, affecting their physiology, fitness and survival, mostly (but not always) in a negative way [4-6]. The consequences of ocean acidification for marine food webs, ecosystems, biogeochemistry and the human use of marine resources are, however, much less certain. In particular, ocean acidification is not the only environmental change that organisms will experience in future, since it will occur in combination with other stressors (e.g. increasing temperature and deoxygenation) [7]. The biological effects of multiple stressors occurring together cannot be assumed to be additive; instead, due to interactions, their combined impacts may be amplified (through synergism) or diminished (antagonism). Furthermore, there is now evidence that some – but not necessarily all – organisms may show genetically-mediated, adaptive responses to ocean acidification [8].

This review provides an updated synthesis of the impacts of ocean acidification on marine biodiversity based upon current literature, including emerging research on the geological history of natural ocean acidification events, and the projected societal costs of future acidification. The report takes into consideration comments and feedback submitted by Parties, other Governments and organisations as well as experts who kindly peer-reviewed the report.

1.1 Mandate of this review

The Conference of the Parties to the Convention on Biological Diversity initially raised its concern on the potential adverse impacts of ocean acidification at its 9th meeting (COP 9; Bonn, 2008), which instigated the CBD Secretariat's first review on this topic "Scientific Synthesis of the Impacts of Ocean

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* pH is defined as the decimal logarithm of the reciprocal of hydrogen ion activity in a solution. Different scales are possible, depending on buffer standards. For seawater, the 'total scale' (pH_T) is now preferred, and most data given in this report can be assumed to be on that basis.

Acidification on Marine Biodiversity" (Technical Series No. 46) [9], carried out jointly with the UNEP World Conservation Monitoring Centre. In response to that review, COP 10 (Nagoya, 2010) recognised ocean acidification as a new and important issue, for consideration as an ongoing activity under the programme of work on marine and coastal biodiversity (decisions X/13 and X/29) and included ocean acidification in the Strategic Plan for Biodiversity 2011-2020 and the Aichi Biodiversity Targets (target 10; X/2).

In decision X/29, the Conference of the Parties to the Convention established a series of expert review processes, in collaboration with various relevant organizations, to assess the impacts of ocean acidification on marine biodiversity. To initiate implementation of the request in this decision, an Expert Meeting on Ocean Acidification was convened by CBD Secretariat, in collaboration with Intergovernmental Oceanographic Commission-UNESCO, in Montreal in October 2011, involving representatives from Parties and relevant organizations. The Expert Meeting identified gaps and barriers in existing monitoring and assessment of ocean acidification in the context of global policy processes; developed options for addressing those gaps and barriers; and considered the need for additional collaborative activities. The workshop report [10] was considered at CBD COP 11 (Hyderabad, 2012), when Parties decided that a new systematic review should be prepared as the basis for further policy action.

The updated synthesis – this document – should provide "a targeted synthesis of the biodiversity implications of ocean acidification for marine and coastal systems, including information on the less reported paleo-oceanographic research, building upon the synthesis provided in CBD Technical Report Series No 46" (XI/18, paragraphs 22-24). This review will be considered by SBSTTA 18 prior to COP 12 in 2014, with a view to forwarding it to Parties, other Governments and relevant organizations and transmitting it to the Secretariat of the United Nations Framework Convention on Climate Change.

In response to a request to Parties to assist in implementing COP 11 decisions, the government of the United Kingdom of Great Britain and Northern Ireland has provided the main financial support for preparing the updated synthesis, through the UK Ocean Acidification research programme, co-funded by the Natural Environment Research Council, the Department for Environment, Food and Rural Affairs, and the Department for Energy and Climate Change. The scientific authorship of this review is, however, fully international, involving contributors from 12 countries, many of whom also participated in the 2011 Expert Meeting. In developing the review, the authors considered 'biodiversity implications' to encompass impacts on marine ecosystems and wider environmental considerations (i.e. consistent with the relatively broad definition of biodiversity in Article 2 of the CBD Convention) [11], rather than limiting the term to quantified measures of species richness, heritable variation, or habitat diversity.

The increasing international awareness of ocean acidification and its societal implications were demonstrated at the 14th meeting of the UN Open-ended Informal Consultative Process (ICP) on Oceans and Law of the Sea (New York, 17-20 June 2013) [12]. At the 14th ICP meeting, an early draft of this CBD review was presented and discussed at a side event convened by CBD Secretariat, in collaboration with the IOC-UNESCO, and valuable feedback was received. The UN General Assembly recognised the attention given to ocean acidification by the 14th ICP meeting and committed itself to continue to pay attention to this important issue, including taking account of the ongoing work of the recently-established Ocean Acidification International Coordination Centre of the International Atomic Energy Agency (A/RES/68/70, para 156; also see Box 2.1 and Table 2.1 below).

1.2 What is ocean acidification?

Ocean acidification can be defined in relatively narrow terms, limiting its meaning to a global-scale, longterm decrease in seawater pH, which currently is primarily due to the human-driven increase in atmospheric CO_2, that is near-certain to intensify. The CO_2-pH relationship has now been observed at many locations, with the longest atmospheric CO_2 time series from the Mauna Loa observatory and a nearby oceanic time series (Figure 1.1).

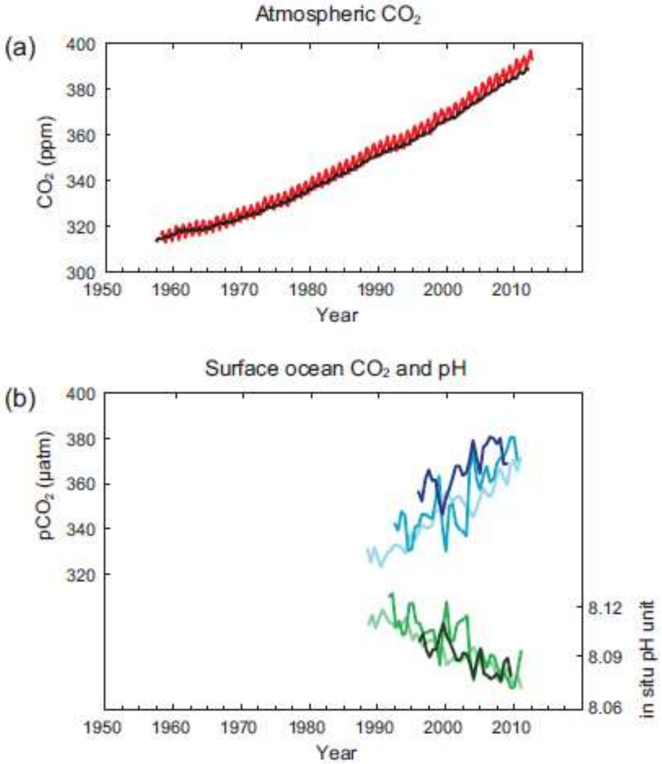

Figure 1.1. Multiple observed indicators of a changing global carbon cycle: (a) atmospheric concentrations of carbon dioxide (CO2) from Mauna Loa (19°32'N, 155°34'W – red) and South Pole (89°59'S, 24°48'W – black) since 1958; (b) partial pressure of dissolved CO2 at the ocean surface (blue curves) and in situ pH (green curves), a measure of the acidity of ocean water. Measurements are from three stations from the Atlantic (29°10'N, 15°30'W – dark blue/dark green; 31°40'N, 64°10'W – blue/green) and the Pacific Oceans (22°45'N, 158°00'W − light blue/light green). Full details of the datasets shown here are provided in the underlying report of the Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change I and the Technical Summary Supplementary Material [13]*.

The above definition of ocean acidification focuses on the reaction of dissolved anthropogenic CO_2 with water to form carbonic acid (H_2CO_3), that dissociates to form bicarbonate ions (HCO_3^-) and hydrogen ions (H^+, quantified by the pH scale). An additional reaction with carbonate ions (CO_3^{2-}; naturally occurring in seawater) also occurs, reducing their concentration. All these reactions are in dynamic equilibrium (Figure 1.2). As a result, the process of ocean acidification can more generally be considered as changes to the seawater 'carbonate system'. Whilst pH values are of great interest, it is not straightforward to measure them with high precision. Instead they are often calculated from other measured parameters, such as dissolved carbon dioxide (pCO_2), total dissolved inorganic carbon (DIC) and total alkalinity (TA; the combined abundance of proton-acceptors, i.e. negatively-charged ions that react with strong acid).

One further chemical reaction is noteworthy. As the abundance of carbonate ions in seawater declines, it affects the stability of calcium carbonate ($CaCO_3$) in solid form, that may be present as bedrock (such as chalk or limestone), dead shells, or as an exterior covering or structural component of living organisms – such as molluscs (e.g. mussels, oysters and sea-snails), echinoderms (e.g. sea urchins), crustaceans (e.g. crabs and lobsters), warm and cold-water corals, and calcifying algae. Such calcifying organisms require more energy to produce $CaCO_3$ in water with lower pH, but they may also experience shell dissolution, unless their exoskeletons and carapaces are protected by an organic layer.

Whether or not such dissolution occurs is determined by the saturation state (Ω) of carbonate, defined as the ratio between dissolved abundances of calcium and carbonate ions and their solubility product

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* Note: The final version of this report may contain a revised version of this figure that will overlap the data shown in these two separate graphs into one graph. Appropriate permissions will be sought from the IPCC before doing so.

constants, the latter being temperature-specific. Thus Ω values need to be greater than 1.0 for unprotected $CaCO_3$ to be stable, and Ω values in the range 3.0 - 5.0 are generally considered optimal for bio-calcification to occur. Currently, the vast majority of the surface ocean is supersaturated with respect to $CaCO_3$, i.e. $\Omega > 1.0$. However, most of the deep ocean is unsaturated, with $\Omega < 1.0$, owing to changes in temperature and pressure (increasing solubility product constants) and the accumulation of biologically produced CO_2 through decomposition (reducing carbonate ion abundance). The depth at which $\Omega = 1.0$ is the saturation horizon, with most of the deep ocean below that horizon and therefore corrosive to unprotected $CaCO_3$. Some calcareous material may be found below that depth if the rate of its supply from the surface or mid-waters exceeds the rate of its dissolution; however, it is very unlikely to be preserved in the fossil record. The few shelled organisms that survive below the saturation horizon have well-protected shells and/or are limited to niche habitats e.g. hot vents [17].

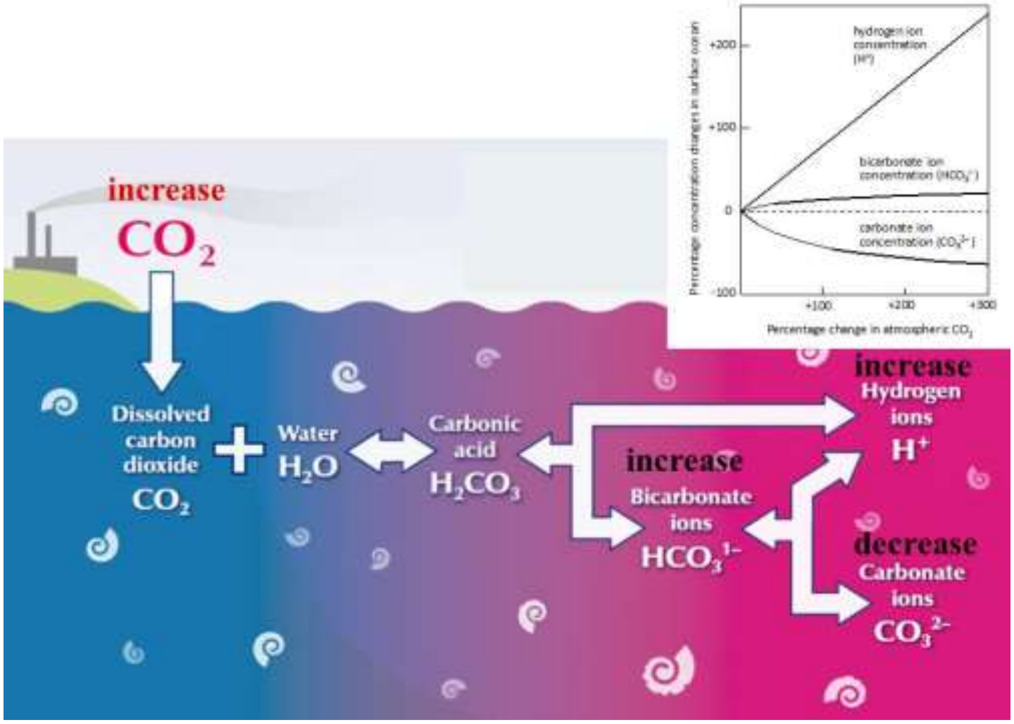


Figure 1.2. The chemical reactions that occur when additional carbon dioxide dissolves in seawater, with net effect of increasing the abundance of hydrogen ions and bicarbonate, whilst reducing carbonate. Inset graph: Model-based global estimates of the percentage changes in hydrogen ions, bicarbonate ions and carbonate ions as mean values in the upper ocean as a result of increases in atmospheric CO_2 of up to 300% on a ~100 year timescale. This model is relatively unsophisticated (e.g. not allowing for temperature and circulation effects), and the results should be considered illustrative of the processes occurring in the main part of this figure. Images, redrawn from [14] and [15]; graph based on data in [16].

An additional complication is that there are two main bio-mineral forms of $CaCO_3$, aragonite and calcite, with the former being slightly more soluble. Thus Ω values for aragonite (and aragonite saturation horizons) differ slightly from those for calcite, and the form of the mineral in different marine species affects their sensitivity to ocean acidification.

Due to different water mass characteristics, the depth of saturation horizons varies naturally between ocean basins. However, it is currently decreasing everywhere, and will continue to do so, as more anthropogenic CO_2 enters the ocean. By the end of this century, aragonite saturation horizons are projected to shallow from >2000 m to ~100 m in the North Atlantic, from ~150 m to the near-surface in the North Pacific [18], and to reach the surface in the Arctic and Southern Ocean [19]. Due to lower temperatures in polar regions, the shallowing of saturation horizons is more pronounced there, an effect described in more detail in Chapter 3.

Aquatic organisms (particularly microbes) have evolved to survive under a wide range of environmental pH conditions, from alkaline lakes to deep sea vents. Thus extremophile algae, fungi and archaea can tolerate pH values as low as 0.5, whilst bacteria, protists and rotifers can survive at pH values as high as 10.5 [20]. Nevertheless, all species have their individual optimal pH ranges and tolerance limits that usually closely match the range of variability naturally encountered in species' habitats.

As discussed in greater detail in Chapter 3, natural seawater pH values can vary greatly over seasonal, daily or annual timescales, and given this variability, it might be thought that the projected pH reduction of ~0.3 during the current century is unlikely to have substantive biological consequences, at least in coastal waters. However, an analogous situation applies to temperature tolerances and projected global warming. A global surface temperature increase of ~2°C is now generally recognised as having 'dangerous' climatic and ecological consequences, increasing extinction risk for many species – despite very many organisms experiencing seasonal (or even daily) temperature ranges that are 5-10 times greater. It is key to note that it is not just an absolute value of pH change which is important, but also the change in potential range and variability. Other important framework considerations relating to the effects of ocean acidification on biodiversity include the following:

- In the same way that global warming is not limited to temperature change, ocean acidification is not limited to pH change. Organisms can respond to changes in any one of the components of the carbonate chemistry system (Figure 1.2), and calcification is not the only process that may be affected. In particular, calcifying algae demonstrate the potential for opposite responses to different components: if there is sufficient light and nutrients, their photosynthesis (and growth rates) may benefit from higher CO_2 or bicarbonate; however, their calcification may be negatively impacted by decreased pH, occurring at the same time. Note that decreased calcification under conditions of ocean acidification is unlikely to be directly due to the reduced availability of carbonate, since most calcifiers take up bicarbonate ions from seawater [21].

- Even within closely related taxa, not all organisms respond similarly to ocean acidification under experimental conditions, and different stages in the life cycle may show different sensitivities [5, 16]. These mixed responses (together with the complexity of marine ecological interactions) make it difficult to develop a quantitative, model-based understanding of the impacts of projected ocean acidification on communities, food webs, ecosystems and the services they provide to society (Figure 1.3). Nevertheless, recent meta-analyses [6][22] on individuals and taxa have identified general trends, consistent taxonomic patterns (Figure 1.4) and life-cycle effects, discussed in detail in Chapter 5.

- Ocean acidification has the potential to change the chemical speciation and solubility of metals and other elements in seawater. The pH sensitivity of boron species is noteworthy, affecting the isotopic composition of boron in biominerals, that can be used ion paleo-pH reconstructions (see Chapter 4). Boron-borate changes can also affect low-frequency sound transmission, with concerns that future pH reductions would make the ocean noisier, with biological impacts e.g. on the behaviour of marine mammals [23]. However, additional physically-based analyses indicate that the problem seems unlikely to be significant [24,25].

- Marine organisms are currently subject to many other environmental changes, in addition to ocean acidification, with the potential to degrade or disrupt ecosystems. Most of these drivers are directly or indirectly due to human activities; they can be broadly grouped into local/regional stressors, e.g. due to over-fishing, habitat loss/destruction, pollution, and enhanced nutrient loading (with associated eutrophication and low oxygen), and global-scale, climate-related impacts, mostly temperature-driven, such as changes in stratification, mixing and other circulation changes, reduced high latitude surface salinity (due to ice melt and river run-off), de-oxygenation and increased ultra-violet (UV) radiation. Key issues relating to the three main global-scale stressors – acidification, warming, and de-oxgenation – are summarised in Table 1.1. Further information on our relatively limited understanding of the interaction of ocean acidification with other factors is given in subsequent chapters.

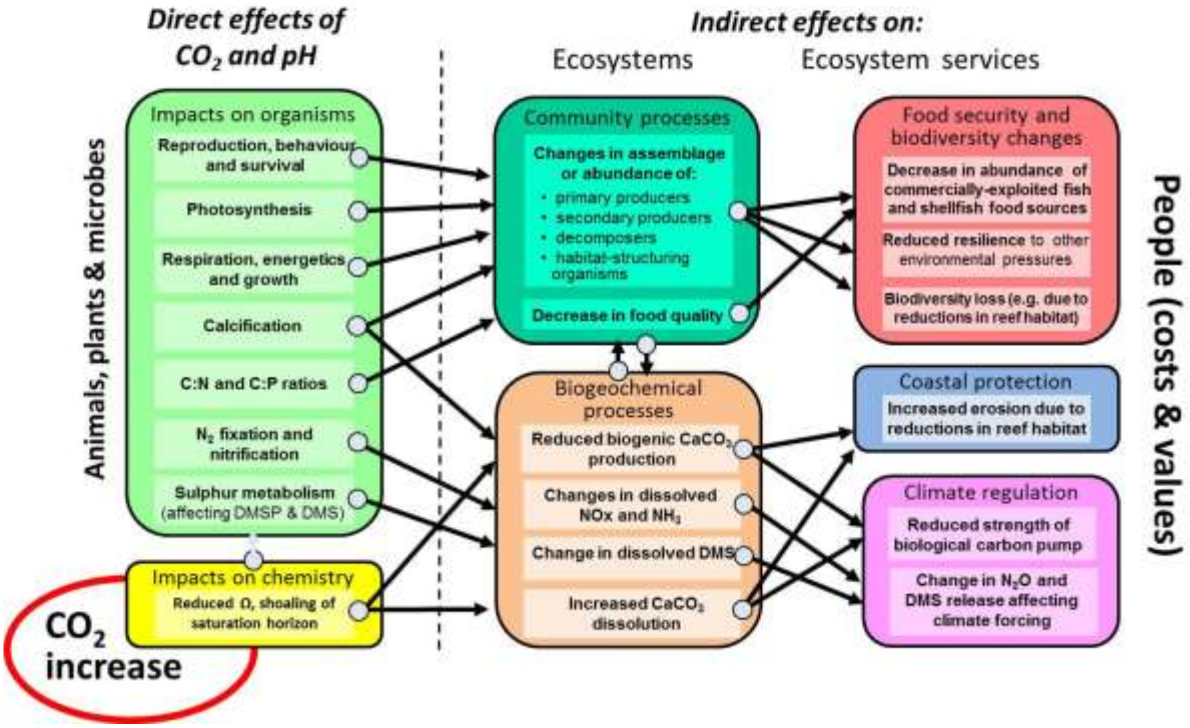


Figure 1.3. Simplified summary of ocean acidification impacts upon organisms, ecosystems, ecosystem services and hence society. Impacts cascade through marine ecosystems with societal effects including changes to food security, biodiversity, coastal protection and climate regulation (see Table 5.2 for further detail). DMS, dimethylsulphide; DMSP, dimethylsulphoniopropionate; Ω, $CaCO_3$ saturation state. Based on [15].

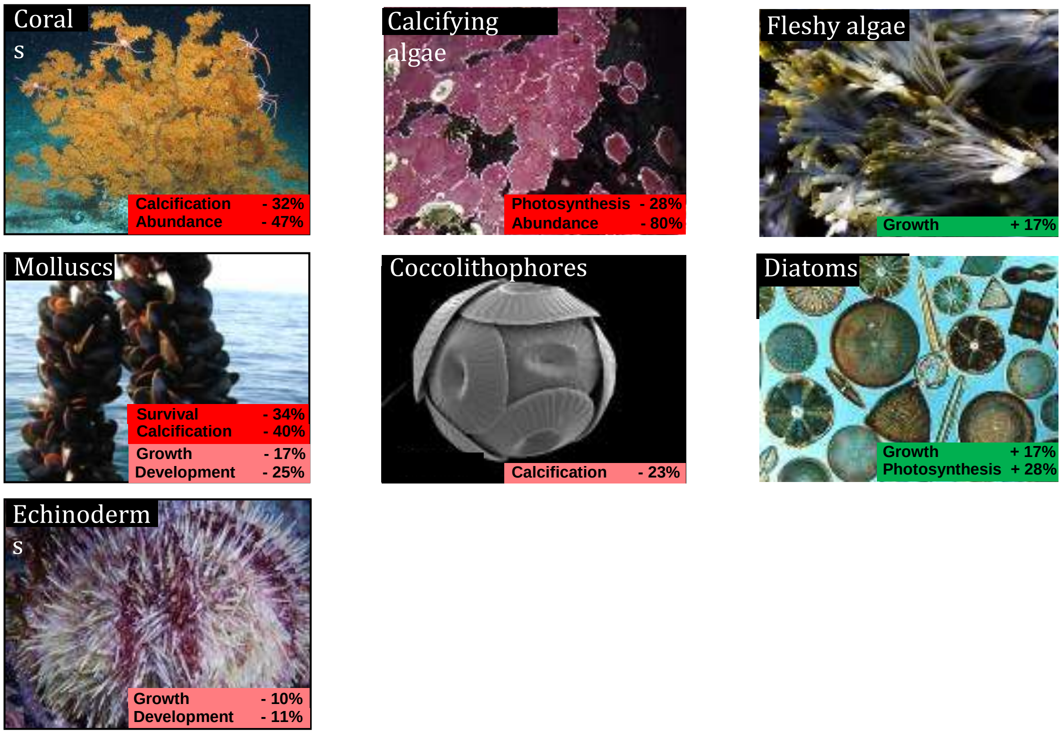


Figure 1.4. Summary of main effects of decrease of 0.5 pH units on taxa showing greatest sensitivity, based on metadata analysis from 228 experimental studies. From [6]

Table 1.1. Summary of the causes and impacts of the three main global-scale stressors that will increasingly affect marine biodiversity, with severity of impacts depending on future emissions of greenhouse gases. Note that there may be reinforcing or ameliorating interactions (synergies or antagonisms) for biological responses to these stressors, and that there are likely to be additional interactions with a wide variety of other environmental parameters, at both the global and local scales. Based on [26] also see [7].

Stressor	**Causes**	**Result**	**Direct effects**	**Impacts *including climatic feedback***
Acidification	• Increasing CO_2 in atmosphere • Some local contributions (eutrophication, industrial emissions)	• Change in ocean pH and carbonate chemistry • Progressive dissolution of calcium carbonate	• Reduced calcification and growth in many species • Reef erosion • Changes in carbon: nitrogen ratio	• Reduced abundance of calcifying species; other food web changes • Effects on aquaculture and human food supply • Risk of coral extinctions, with habitat loss and increased coastal erosion • *Reduced ocean uptake of* CO_2 • *Potential warming feedback via DMS and cloud formation*
Warming	• Increasing greenhouse gases in atmosphere	• Temperature increase • Less ocean mixing due to increased stratification • Loss of polar sea ice • More freshwater run-off in polar regions (reducing salinity) • Sea-level rise	• Reduced solubility of CO_2, O_2 and calcium carbonate • Reduced productivity where more stratified; increased productivity in Arctic • Physiological effects on organisms (metabolism, growth and survival)	• Poleward shift of (mobile) species' ranges • Coral bleaching • Changes in community composition and food webs • Global reduction in marine productivity • *Reduced ocean uptake of* CO_2 • *Reduced carbon export to ocean interior*
De-oxygenation	• Warming reduces O_2 solubility • Stratification reduces O_2 supply to ocean interior • Local causes: eutrophication	• Reduced O_2 availability for respiration, especially in productive regions and mid/deep water	• Slower metabolism and growth of zooplankton and fish	• Effects on abundances and distributions • Shift to organisms tolerant to low O_2 (mostly microbial) • Reduced fishery yield • *Increased marine production of methane and nitrous oxide (greenhouse gases)*
All three together	• Increasing CO_2 and other greenhouse gases	• Combined stress of reduced pH, warming and low dissolved O_2	• Damage to organism physiology and energy balance • Disrupted food webs	• Major changes to ocean physics, chemistry and biology • Biodiversity loss, with impacts on ecosystem services • *Risk of multiple positive feedbacks, increasing rate of future climate change*

1.3 Re-visiting key knowledge gaps identified in the previous CBD review

The concluding chapter ("Uncertainties and other considerations") of the 2009 CBD review of ocean acidification [9] identified five questions to assist in focussing research effort on important knowledge gaps. Table 1.2 below briefly re-visits these issues, summarising relevant progress and the current status of our understanding of these topic areas. Additional detail, with supporting scientific citations, is given in subsequent chapters of this review.

Three generic comments can be made on the 2009 research questions. Firstly, all five questions refer to calcification or calcifiers, whereas there is now greater appreciation that a much wider range of physiological and biogeochemical processes, and organisms, may be affected (Figures 1.3, 1,4) – whilst also recognising that the scale and importance of many of these additional impacts are still very uncertain. Second, these questions only indirectly refer, through adaptation (Q3), to the relevance of genetic and evolutionary processes in determining the scale of future acidification impacts. Such issues are now being given much greater attention [8]. Third, none of the questions explicitly mentions ecosystem services, societal impacts or possible policy responses. Whilst research and understanding in these areas are not yet well-developed, the current review does include some consideration of the 'human dimensions' of ocean acidification and its effects on biodiversity.

Table 1.2. Knowledge gaps identified in 2009 [9] and subsequent relevant research developments.

Research question	Summary of recent research progress; other comments
1. How is calcification affected in organisms at different stages of their life cycle?	Significant progress made on life-cycle experimental studies. For many species of echinoderms, acidification slows development of embryos/larvae (hence likely to increase mortality in field); juveniles may also be negatively affected, whilst adults are generally more tolerant. Life-cycle changes in acidification sensitivity not limited to calcifiers. Increased awareness that experimental life-cycle studies should be relevant to natural conditions, with need for 'realistic' (yet well-controlled) pH/carbonate system parameters and controlled food availability. Potential impacts and interactions of multiple stressors (e.g. temperature, nutrients/food, oxygen) require further study.
2. Why do some calcifying organisms seem to be less affected than others?	Increased appreciation that variability of response can be due to: i) different organisms responding to different aspects of carbonate chemistry (CO_2, pH, carbonate, bicarbonate and saturation state); ii) non-standard experimental methods (inter-comparability now much improved through 'best practice' protocol development and improved international liaison); iii) confounding effects of other, non-controlled factors (nutrient/food availability; light for phytoplankton studies; seasonal cycles affecting physiology and metabolism); and iv) inherent response variability, between strains, species and higher taxonomic groups.
3. How is adaptation and survival influenced by the different mechanisms of calcification or other physiological factors?	This question covers many research topics, not only biological control of the calcification process (that differs between different groups), but also the scope for genetic adaptation on decadal-to-century timescales. Scope for adaptation – that is difficult to determine, but can be informed by paleo-studies - is dependent on reproductive strategy, existing genotypic variability (on which selection can operate), and generation time. Such adaptation may be at cost of reduced fitness for other traits, and recent research documents the best approaches for tackling this challenging issue [8,27]. Text on this question in the 2009 report focussed on potential impacts on pteropods (planktonic molluscs, also known as sea butterflies): several new experimental and field studies on this group have confirmed their vulnerability to near-future changes in polar water chemistry.
4. How do other environmental factors such as carbonate concentration, light levels, temperature and nutrients affect calcification processes?	There is considerable overlap of this question with the others above, since it addresses the (multi-stressor) context in which acidification occurs, influencing not only calcification but other physiological processes. In the past 5 years, there have been many two-factor studies (mostly with temperature as second variable), providing important insights on potential interactions. However, very few experiments control three or more variables: whilst such studies are needed, their design, implementation and interpretation are not straightforward. Mesocosms and natural gradients provide alternative approaches to resolving issues of environmental complexity.
5. How will communities with a mixture of calcifying and non-calcifying organisms respond to decreasing calcification rates, and what impact will this have on the marine food chain?	Determination of ecosystem level effects is extremely demanding, and remains an overall goal – taking account of other processes affected by acidification (Figure 1.3), in addition to calcification. Model-based approaches provide scenario-based projections, over a range of spatial and temporal scales, and these can be used for risk-based policy action; however, models cannot be expected to give single answer, definitive predictions. In particular, model outputs will necessarily depend on assumptions regarding future CO_2 emissions, as well as the future scale and influence of other environmental variables. Furthermore, models are unable to take account of factors (e.g. genetic adaptation) that have not yet been well-quantified.

1. Doney SC, Fabry VJ, Feely RA, Kleypas JA (2009) Ocean acidification: the other CO_2 problem. Annual Review of Marine Science 1: 169-192.
2. Sabine CLCL, Feely RARA, Gruber N, Key RMRM, Lee K, et al. (2004) The oceanic sink for anthropogenic CO2. Science 305: 367-367.
3. Feely RA, Sabine CL, Lee K, Berelson WM, Kleypas JA, et al. (2004) Impact of anthropogenic CO_2 on the $CaCO_3$ system in the oceans. Science 305: 362.
4. Gattuso JP, Hansson L (2011) Ocean Acidification. Oxford: Oxford University Press.
5. Wicks LC, Roberts JM (2012) Benthic invertebrates in a high-CO_2 world. Oceanography and Marine Biology: An Annual Review 50: 127-188.
6. Kroeker KJ, Kordas RL, Crim R, Hendriks IE, Ramajo L, et al. (2013) Impacts of ocean acidification on marine organisms: quantifying sensitivities and interaction with warming. Global Change Biology 19: 1884-1896.
7. Bijma J, Portner HO, Yesson C, Rogers AD (2013) Climate change and the oceans - What does the future hold? Marine Pollution Bulletin 74: 495-505.
8. Sunday JM, Calosi P, Dupont S, Munday PL, Stillman JH, et al. (2014) Evolution in an acidifying ocean. Trends Ecol Evol 29: 117-125.
9. Secretariat of the Convention on Biological Diversity. Scientific synthesis on the impacts of ocean acidification on marine biodiverstiy,. 2009 Montreal. 61 p
10. Convention on Biological Diversity.(2012) Report of the expert meeting to develop a series of joint expert review processes to monitor and assess impacts of ocean acidification on marine and coastal biodiversity. UNEP/CBD/SBSTTA/16/INF/14
11. Convention on Biological Diversity. CBD Convention.
12. Report on the work of the UN Open-ended Informal Consultative Process on Oceans and Law of the Sea at its 14th meeting. Letter dated 17 July 2013 from the Co-Chairs of the Consultative Process addressed to the President of the General Assembly.

2013.http://www.un.org/Depts/los/consultative_process/consultative_process.htm; see also http://www.un.org/Depts/los/general_assembly/general_assembly_reports.htm
13. IPCC (2013) Twelfth Session of Working Group I, Summary for Policymakers.
14. Laffoley D, Baxter JM, editors (2010) Ocean Acidification Reference User Group: European Project on Ocean Acidification (EPOCA).
15. Williamson P, Turley C (2012) Ocean acidification in a geoengineering context. Philosophical Transactions of the Royal Society a-Mathematical Physical and Engineering Sciences 370: 4317-4342.
16. The Royal Society.(2005) Ocean acidification due to increasing atmospheric carbon dioxide. London: Royal Society
17. Tunnicliffe V, Davies KTA, Butterfield DA, Embley RW, Rose JM, et al. (2009) Survival of mussels in extremely acidic waters on a submarine volcano. Nature Geoscience 2: 344-348.
18. Guinotte JM, Orr JC, Cairns S, Freiwald A, Morgan L, et al. (2006) Will human-induced changes in seawater chemistry alter the distribution of deep-sea scleractinian corals? Frontiers in Ecology and the Environment 4: 141-146.
19. Feely RA, Sabine CL, Byrne RH, Millero FJ, Dickson AG, et al. (2012) Decadal changes in the aragonite and calcite saturation state of the Pacific Ocean. Global Biogeochemical Cycles 26.
20. Rothschild LJ, Mancinelli RL (2001) Life in extreme environments. Nature 409: 1092-1101.
21. Roleda MY, Morris JN, McGraw CM, Hurd CL (2012) Ocean acidification and seaweed reproduction: increased CO2 ameliorates the negative effect of lowered pH on meiospore germination in the giant kelp Macrocystis pyrifera (Laminariales, Phaeophyceae). Global Change Biology 18: 854-864.
22. Wittmann AC, Portner H-O (2013) Sensitivities of extant animal taxa to ocean acidification. Nature Climate Change 3: 995-1001.
23. Ilyina T, Zeebe RE, Brewer PG (2010) Future ocean increasingly transparent to low-frequency sound owing to carbon dioxide emissions. Nature Geoscience 3: 18-22.
24. Reeder DB, Chiu CS (2010) Ocean acidification and its impact on ocean noise: Phenomenology and analysis. Journal of the Acoustical Society of America 128: El137-El143.
25. Joseph JE, Chiu CS (2010) A computational assessment of the sensitivity of ambient noise level to ocean acidification. Journal of the Acoustical Society of America 128: El144-El149.
26. Turley CM, Keizer T, Williamson P, Gattuso JP, Ziveri P, et al. Hot, Sour and Breathless – Ocean under stress. 2013: Plymouth Marine Laboratory, UK Ocean Acidification Research Programme, European Project on Ocean Acidification, Mediterranean Sea Acidification in a Changing Climate project, Scripps Institution of Oceanography at UC San Diego, OCEANA. 6 p
27. Reusch TB, Boyd PW (2013) Experimental evolution meets marine phytoplankton. Evolution 67: 1849-1859.

2. SCIENTIFIC AND POLICY FRAMEWORK

2.1 Steps toward global recognition and international science collaboration

Ocean acidification is a relatively young field of research. The first results from laboratory experiments on the effects on marine organisms appeared in the late 1990s. These built upon early landmark studies showing that the uptake of anthropogenic CO_2 decreased ocean buffering capacity [1], and that this could decrease calcification [2,3] by marine organisms. Scientific interest in ocean acidification – not only by chemists and physiologists, but also by ecologists, biogeochemists, paleontologists and economists – has increased exponentially in the past few years, with a fifteen-fold increase in the number of publications from 2004 to 2012, and an increasing number of new researchers entering the field (Figure 2.1) [4,5].

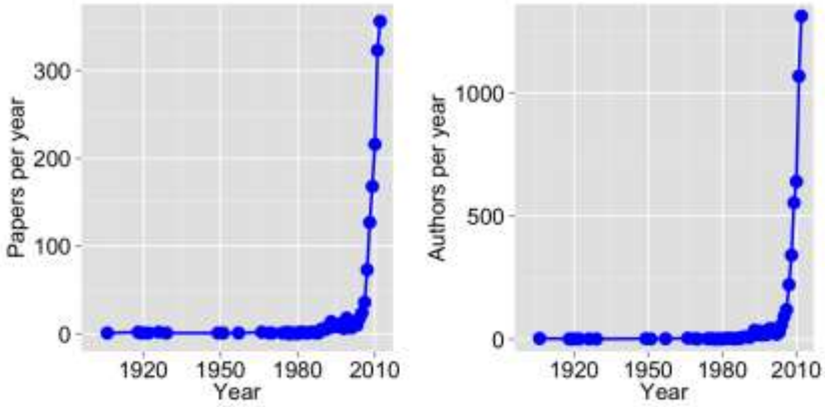
Key Messages: Chapter 2

1. Research interest and political awareness of ocean acidification have increased exponentially in the past few years

2. International cooperation and interdisciplinary research have helped to advance the science of ocean acidification

3. Many intergovernmental bodies have initiated activities on ocean acidification

The prioritisation of ocean acidification as a research topic began around 2003-04, with its inclusion in the Science Plans of two global change research programmes, the Surface Ocean Lower Atmosphere Study (SOLAS) [6] and the Integrated Marine Biogeochemistry and Ecosystem Research project (IMBER) [7]. In a closely-related initiative, the first symposium on “The Ocean in a High CO_2 World” was held in Paris in 2004, convened by the Scientific Committee on Oceanic Research (SCOR), the Intergovernmental Oceanographic Commission of the United Nations Educational, Scientific and Cultural Organization (IOC-UNESCO) and the International Geosphere-Biosphere Programme (IGBP).



	2004	2005	2006	2007	2008	2009	2010	2011	2012
papers	18	24	36	73	127	168	216	323	356
authors	58	92	120	221	341	554	640	1068	1312

Figure 2.1. The annual number of ocean acidification peer-reviewed publications and the number of authors involved 1900-2012. Data from the bibliographic database of the IAEA Ocean Acidification International Coordination Centre (OA-ICC), updated from Gattuso and Hansson[4,5]

However, wider awareness of ocean acidification remained extremely low until the Royal Society’s 2005 report “Ocean acidification due to increasing atmospheric carbon dioxide” [8]. Several other policy-related publications have subsequently attracted significant attention, including:

- The 2008 Monaco Declaration [9], signed by 155 scientists from 26 countries and endorsed by HSH Prince Albert II of Monaco. The declaration called upon policymakers to support initiatives in multi-disciplinary research, communication and policy action. It arose from the second symposium on the "The Ocean in a High CO_2 World", held in Monaco and co-organised by the International Atomic Energy Agency (IAEA).

- The CBD's 2009 report "Scientific Synthesis of the Impacts of Ocean Acidification on Marine Biodiversity" [10], produced jointly with the United Nations Environment Programme (UNEP) World Conservation Monitoring Centre. Aspects of that report have already been discussed in Chapter 1.

- The 2009 statement on ocean acidification by the InterAcademy Panel on International Issues (IAP) [11], endorsed by over 100 academies of science worldwide. This called on world leaders to respond to the emerging threat of ocean acidification by taking action to reduce CO_2 emissions and mitigate damage to marine ecosystems.

- "Ocean Acidification Summary for Policymakers"[IGBP, IOC, SCOR 2013] arising from the 3rd Ocean in a High-CO_2 World symposium, held in Monterey, USA in 2012.

- The 2013 assessment of Arctic Ocean acidification [AMAP, 2013] and its societal implications, carried out by the Arctic Monitoring and Assessment Programme (AMAP)[12].

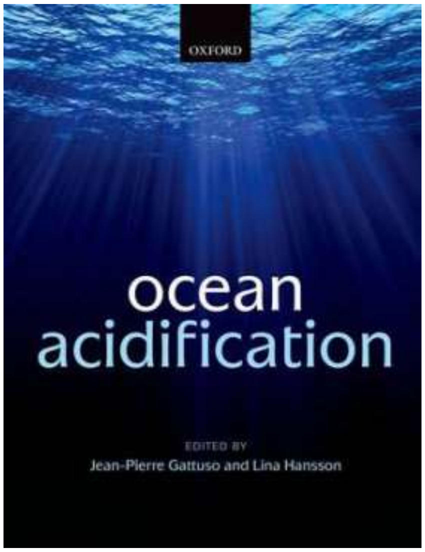


Figure 2.2. The first book on ocean acidification, with inter-national authorship and arising from the European EPOCA project.

The first large-scale, multi-national project on ocean acidification was the European Commission's "European Project on Ocean Acidification" (EPOCA) [13], 2008-2012. EPOCA brought together more than 160 scientists from 32 countries to address scientific uncertainties on ocean acidification, including biogeochemical modelling, biological effects and implications for marine biodiversity. A notable output was publication of the book "Ocean Acidification" [5] in 2011 (Figure 2.2). A second EC project on ocean acidification has focused on its links to climate change in the Mediterranean (MedSeA) [14], 2011-2014.

National research efforts, many with close linkages to international programmes, have included the German programme Biological Impacts of Ocean Acidification (BIOACID) [15], that started in 2009, and is now in its 2nd funding phase; US research support (via NSF and NOAA), mandated by the 2009 Federal Ocean Acidification Research and Monitoring (FOARAM) Act [16]; the UK Ocean Acidification Research Programme (UKOA) [17] that began in 2010; and other programmes and, projects in Australia, China, Japan, Republic of Korea, Norway and elsewhere. The current breadth of national involvement in ocean acidification research is indicated in Figure 2.3.

Linkages between these worldwide research efforts on ocean acidification have been encouraged at the intergovernmental level (see 2.2 below), also by national funders and by non-governmental science bodies, particularly by the SOLAS-IMBER Ocean Acidification Working Group (SIOA-WG) [18]. The SIOA-WG helped to establish the Ocean Acidification International Coordination Centre (OA-ICC) [19] of the IAEA, based in Monaco.

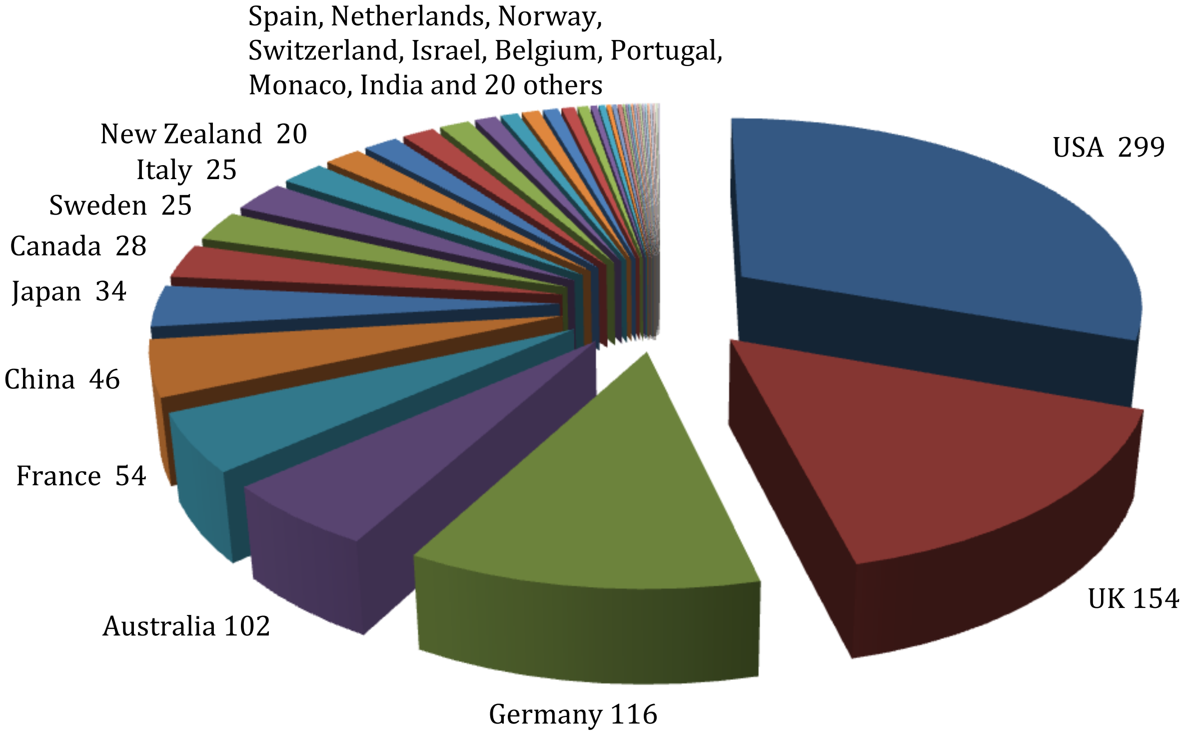


Figure 2.3. National involvement in ocean acidification research, based on first authors' addresses for peer-reviewed papers published in 2005-2012 (OA-ICC data)[4].

The OA-ICC became operational in 2012, supported by IAEA member states; its activities include the facilitation of global observation and monitoring; joint-use research platforms and experiments; definition of best practices; data management; capacity building; dissemination and outreach. OA-ICC liaison with policy-makers, the private sector and other stakeholders is assisted by the Ocean Acidification international Reference User Group (OA-iRUG). This body, re-constituted in 2013, was originally established in 2008 through the EPOCA project; it involves scientists and research users from industry, government and non-governmental organizations. OA-iRUG publications [20] aim to provide key policy-relevant messages on ocean acidification to decision makers.

The most recent initiative to enhance international science collaboration has been the development of the Global Ocean Acidification Observing Network (GOA-ON), supported by the OA-ICC, IOC-UNESCO, the Global Ocean Observing System (GOOS), the International Ocean Carbon Coordination Project (IOCCP) and national funding agencies. Further details are given in Section 3.3.

2.2 Intergovernmental interest in ocean acidification and actions to date

Whilst some local and national policy measures can be taken to address ocean acidification impacts (e.g., formation of a Marine Resources Advisory Council by the State of Washington, USA, charged with safeguarding its shellfish industry against ocean acidification [21], ocean acidification is essentially a global problem – requiring a global, intergovernmental policy response. At the United Nations Conference on Sustainable Development "Rio+20" (Rio de Janeiro, June 2012) all stakeholders, including UN bodies, intergovernmental organizations and national governments, were invited to make commitments to deliver concrete results for sustainable development on a voluntary basis. There was substantial stakeholder input to the consideration of ocean acidification resulting in a specific ocean acidification statement (number 166) in the Conference's outcome document "The Future We Want" [22].

> *"We call for support to initiatives that address ocean acidification and the impacts of climate change on marine and coastal ecosystems and resources. In this regard, we reiterate the need to work*

> *collectively to prevent further ocean acidification, as well as to enhance the resilience of marine ecosystems and of the communities whose livelihoods depend on them, and to support marine scientific research, monitoring and observation of ocean acidification and particularly vulnerable ecosystems, including through enhanced international cooperation in this regard."*

One of the main outcomes of the Rio+20 Conference was the agreement by member States to launch a transparent intergovernmental process to develop a set of Sustainable Development Goals (SDGs) to be agreed by the General Assembly at its 68th session (2013 – 2014). The progress report[23] of the Open Working Group of the UN General Assembly tasked with the development of the SDGs includes mention of ocean acidification.

Box 2.1 provides relevant text from the 68th session of the UN General Assembly, recognising ocean acidification as an issue of concern. There have also been actions by several other intergovernmental bodies and organizations, mostly within the UN system, to inform policy makers and support policy development [24] as summarised in Table 2.1. Note that no single UN body currently has a designated lead role for policy development regarding ocean acidification, and there is ongoing debate [25,26] on this issue, particularly with regard to the linkage to the regulatory framework for CO_2 emission reductions. CBD's own major role in raising awareness of ocean acidification and other association actions has already been covered in Chapter 1, and is only briefly re-presented in Table 2.1.

Box 2.1. Extracts from Resolution 68/70 of the United Nations General Assemby (passed on 9 December 2013) giving specific mention to ocean acidification. The General Assembly is the main deliberative, policy-making and representative organ of the UN.

Paragraph 17

called upon States and international financial institutions, including through bilateral, regional and global cooperation programmes and technical partnerships, to develop capacity-building activities in and to transfer to developing countries, in particular least developed countries and small island developing States, on mutually agreed terms, and taking into account the Intergovernmental Oceanographic Commission Criteria and Guidelines on the Transfer of Marine Technology, environmentally sound technologies to study and minimize the impacts of ocean acidification

Paragraph 153

noted the work of the Intergovernmental Panel on Climate Change, including its recent findings on the acidification of oceans, and encouraged States and competent international organizations and other relevant institutions, individually and in cooperation, to urgently pursue further research on ocean acidification, especially programmes of observation and measurement, noting in particular the continued work of the Convention on Biological Diversity and paragraph 23 of decision XI/18 adopted at the eleventh meeting of the Conference of the Parties to the Convention on Biological Diversity, and to increase national, regional and global efforts to address levels of ocean acidity and the negative impact of such acidity on vulnerable marine ecosystems, particularly coral reefs

Paragraph 154

recalled that, in "The future we want", States called for support for initiatives that address ocean acidification and the impacts of climate change on marine and coastal ecosystems and resources and, in this regard, reiterated the need to work collectively to prevent further ocean acidification, as well as to enhance the resilience of marine ecosystems and of the communities whose livelihoods depend on them, and to support marine scientific research, monitoring and observation of ocean acidification and particularly vulnerable ecosystems, including through enhanced international cooperation in this regard

Paragraph 155

noted with concern the approximately 30 per cent increase in the acidity of ocean surface waters since the beginning of the industrial era and the wide range of impacts associated with the continuing and alarming acidification of the world's oceans, and urged States to make significant efforts to tackle the causes of ocean acidification and to further study and minimize its impacts, to enhance local, national, regional and global cooperation in this regard, including the sharing of relevant information, and to take steps to make marine ecosystems more resilient to the impacts of ocean acidification

Paragraph 156

committed itself to continue to pay attention to this important issue, including by taking into account the first global integrated assessment and the ongoing work of the recently established Ocean Acidification International Coordination Centre of the International Atomic Energy Agency

Paragraph 217

recalled that, in “The future we want”, States recognized the significant economic, social and environmental contributions of coral reefs, in particular to islands and other coastal States, as well as the significant vulnerability of coral reefs and mangroves to impacts, including from climate change, ocean acidification, overfishing, destructive fishing practices and pollution, and support international cooperation with a view to conserving coral reef and mangrove ecosystems and realizing their social, economic and environmental benefits, as well as facilitating technical collaboration and voluntary information-sharing

Paragraph 218

encouraged States and relevant international institutions to improve efforts to address coral bleaching by, inter alia, improving monitoring to project and identify bleaching events, supporting and strengthening action taken during such events and improving strategies

Table 2.1. Summary of activities of United Nations subsidiary bodies, Conventions and other intergovernmental organizations in relation to ocean acidification, based on [24]. This list does not claim to be comprehensive. *Body with government membership but not part of the UN.

Body, subsidiary body/agency or Convention; activities			
United Nations Convention on Law of the Sea (UNCLOS)	Treaty which sets out the legal framework within which all activities in the oceans and seas must be carried out		• Part XII of UNCLOS addresses the protection and preservation of the marine environment • Part XIII of UNCLOS addresses marine scientific research
United Nations Division for Ocean Affairs and the Law of the Sea (DOALOS)	*Open-ended Informal Consultative Process (ICP) on Oceans and Law of the Sea*	Forum to facilitate the annual review by the General Assembly of developments in ocean affairs and the law of the sea	• 14th ICP meeting (June 2013) on Impacts of Ocean Acidification on the Marine Environment; report to 2013 UN General Assembly [27]
United Nations Environment Programme ***(UNEP)***	Coordination of UN environmental activities		• 2010 publication: “Environmental Consequences of Ocean Acidification: a Threat to Food Security” [29] • Co-support of 3rd UN Conference on Sustainable Development • Lead for Transboundary Waters Assessment Programme (with UNESCO-IOC and others) that includes assessment of ocean acidification
United Nations Educational, Scientific and Cultural Organization ***(UNESCO)***	*Inter-governmental Oceanographic Commission* *(IOC)*	The UN body for ocean science, observatories, data, information exchange and services	• Coordination of OA-relevant chemical and biological measurements through Global Ocean Observing System (GOOS) and International Ocean Carbon Coordination Project (IOCCP; co-supported by SCOR); support for the Global Ocean Acidification Observing Network (GOA-ON) • Lead for “A Blueprint for Ocean and Coastal Sustainability” [28] (with IMO, FAO and UNDP), including actions to mitigate and adapt to ocean acidification • Major role in developing the Ocean in a High CO_2 World symposium series and the associated Ocean Acidification Summaries for Policymakers (2009 and 2013)
World Meteorological Organization ***(WMO)***	*Intergovernmental Panel on Climate Change* *(IPCC; created with UNEP, advises UNFCCC)*	Assessments of climate change and associated impacts	• Ocean acidification included in IPCC 4th Assessment Report, and in greater detail in 5th Assessment Report (AR5, Working Groups I, II and III) [29,30]. High confidence given to pH decrease of 0.1 in ocean surface water since the beginning of the industrial era.

International Maritime Organization ***(IMO)***	*London Convention and Protocol*	Control of marine pollution through regulation of waste disposal	• Control of sub sea-bed CO_2 sequestration • Development of regulatory framework (within the scope of the Convention and Protocol) for research on ocean fertilization and other marine geoengineering relevant to ocean acidification
International Atomic Energy Agency ***(IAEA)***	Encourage peaceful uses and applications of nuclear technology		• Hosting of Ocean Acidification International Coordination centre (OA-ICC) to assist the worldwide scientific study of ocean acidification • Convening of two workshops (in 2010 and 2012) on socio-economics of ocean acidification • Development, through GOA-ON, of global network to measure changes in ocean carbon chemistry and its ecological impacts • Improving ocean acidification data management; capacity building, dissemination and outreach.
United Nations Framework Convention on Climate Change ***(UNFCCC)***	Legal framework for global reduction in CO_2 emissions, in order to prevent "dangerous anthropogenic interference with the climate system".		• Limited mention of ocean acidification in UNFCCC decisions and documents, but discussed as 'emerging issue' by Subsidiary Body for Scientific and Technical Advice and by associated research dialogue. • Ocean acidification covered by side-events at UNFCCC Conference of Parties since 2009
Convention on Biological Diversity ***(CBD)***	Treaty to promote conservation and sustainable use of biological diversity		• Concern on ocean acidification raised at 9th CBD Conference of Parties (COP 9) in 2008 • 2009 Review (with UNEP) "Scientific Synthesis of the Impacts of Ocean Acidification on Marine Biodiversity" [10] • At COP 10 (2010), ocean acidification included in CBD Strategic Plan for Biodiversity (2011-2020) and Aichi Biodiversity Targets • Expert review process for ocean acidification initiated by Expert Meeting in 2012 and new review.
Convention for Protection of the Marine Environment of the North-East Atlantic* ***(OSPAR)***	Combines and updates Oslo and Paris Conventions, covering "all human activities that might adversely affect the marine environment of the North East Atlantic"		• Concern on ocean acidification expressed in 2012, resulting in establishment (with ICES) of Study Group on ocean acidification; reports published in 2013 and2014 • Development of protocols for ocean acidification monitoring and assessment [31]
Commission for the Conservation of Antarctic Marine Living Resources* ***(CCAMLR)***	Conservation of Antarctic marine life		• Expressed concern on potential impacts of ocean acidification on Antarctic marine life, including effects on krill [32]
Joint Group of Experts on the Scientific Aspects of Marine Environ-mental Protection (GESAMP)	*Sponsored by IMO, FAO, UNESCO-IOC, WMO, IAEA, UNEP, UNIDO and UNDP*	Advises the UN system on scientific aspects of marine environmental protection	• CO_2 considered as pollutant; ocean acidification included in GESAMP contribution to open ocean part of Transboundary Waters Assessment Programme
Arctic Council*	*Arctic Monitoring and Assessment Programme (AMAP)*	Provision of information on status of Arctic environment	• AMAP Arctic Ocean Acidification Assessment (2013) [12,34]
International Union for Conservation of Nature* ***(IUCN)***	Aim is to conserve biodiversity at global and local level		• Work with IOC-UNESCO, Ocean Acidification international Reference User Group and others to raise awareness of ocean acidification.

1. Revelle R, Suess HE (1957) Carbon dioxide exchange between atmosphere and ocean and the question of an increase of atmospheric CO2 during the past decades. Tellus 9: 18-27.
2. Broecker WS, Takahash.T (1966) Calcium carbonate precipitation on Bahama Banks. Journal of Geophysical Research 71: 1575-&.
3. Smith SV, Pesret F (1974) Processes of carbon dioxide flux in Fanning-Island lagoon. Pacific Science 28: 225-245.

4. Data from the bibliographic database of the Ocean Acidification International Coordination Centre (OA-ICC), updated from ref 5; http://www.iaea.org/ocean-acidification/page.php?page=2196
5. Gattuso JP, Hansson L (2011) Ocean Acidification. Oxford: Oxford University Press.
6. IGBP Secretariat. SOLAS (2004) Surface Ocean Lower Atmosphere Study: Science Plan and Implementation Strategy. IGBP Report 50. Stockholm
7. IGBP Secretariat. IMBER (2005) Integrated Marine Biogeochemistry and Ecosystem Study: Science Plan and Implementation Strategy. IGBP Report 52. Stockholm. 76 p
8. The Royal Society. (2005) Ocean acidification due to increasing atmospheric carbon dioxide. London: Royal Society
9. Monaco Declaration (2009). Second Symposium on The Ocean in a High CO2 World 4 p. Monaco: Prince Albert II of Monaco Foundation. http://ioc-unesco.org/index.php?option=com_content&task=view&id=99&Itemid=112
10. Secretariat of the Convention on Biological Diversity. Scientific synthesis on the impacts of ocean acidification on marine biodiverstiy,. 2009 Montreal. 61 p
11. IAP statement on ocean acidification. 2009. http://www.interacademies.net/10878/13951.aspx
12. Arctic Monitoring and Assessment Programme. Oslo, Norway.http://www.amap.no/documents/doc/AMAP-Arctic-Ocean-Acidification-Assessment-Summary-for-Policy-makers/808
13. EPOCA http://www.epoca-project.eu
14. MedSea http://www.medsea-project.eu
15. BIOACID http://www.bioacid.de
16. FOARAM Act http://oceanacidification.noaa.gov/AboutUs/FOARAMAct.aspxwww.bioacid.de
17. UK Ocean Acidification Research Programme http://www.oceanacidification.org.uk
18. IMBER http://www.imber.info/index.php/Science/Working-Groups/SOLAS-IMBER-Carbon/Subgroup-3
19. IAEA http://www.iaea.org/ocean-acidification
20. Ocean Acidification International Reference User Group, 2012. Ocean acidification: the knowledge base 2012. Updating what we know about ocean acidification and key global challenges. 8 p. UK: European Project on Ocean Acidification (EPOCA), UK Ocean Acidification Research Programme (UKOA), Biological Impacts of Ocean Acidification (BIOACID), Mediterranean Sea Acidification in a Changing Climate (MedSeA).http://www.iaea.org/ocean-acidification/page.php?page=2198.
21. Feely RA, Sabine CL, Byrne RH, Millero FJ, Dickson AG, et al. (2012) Decadal changes in the aragonite and calcite saturation state of the Pacific Ocean. Global Biogeochemical Cycles 26.
22. http://www.uncsd2012.org/thefuturewewant.html
23. http://sustainabledevelopment.un.org/content/documents/3238summaryallowg.pdf
24. Herr D, Isensee K, Turley CM (Submitted) International policy on ocean acidification: relevant activities and future needs.
25. Harrould-Kolieb ER, Herr D (2012) Ocean acidification and climate change: synergies and challenges of addressing both under the UNFCCC. Climate Policy 12: 378-389.
26. Kim RE (2012) Is a new multilateral environmental agreement on ocean acidification necessary? Review of European Community and International Environmental Law 21: 243-258.
27. http://www.un.org/depts/los/consultative_process.htm
28. IOC/UNESCO, IMO, FAO, UNDP A blueprint for ocean and coastal sustainability. 2011 Paris.http://www.uncsd2012.org/index.php?page=view&type=510&nr=180&menu=20
29. Field CB, Barros V, Stocker TF, Qin D, Mach KJ, et al. (2011) Workshop Report of the Intergovernmental Panel on Climate Change Workshop on Impacts of Ocean Acidification on Marine Biology and Ecosystems. California, USA: Stanford
30. IPCC (2013). *Climate Change 2013: The Physical Science Basis.* Working Group I Contribution to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change. http: www.ipcc.ch
31. Hydes DJ, McGovern E, Walsham P (2013) Chemical aspects of ocean acidification monitoring in the ICES marine area. ICES Cooperative Research Report 319: 78.
32. CCAMLR–WG-EMM-12/32 Impacts of ocean acidification on Antarctic krill biology: preliminary results and future research direction.
33. UNCSD2012 http://www.uncsd2012.org/thefuturewewant.html
34. Arctic Monitoring and Assessment Programme http://www.amap.no/documents/doc/amap-assessment-2013-arctic-ocean-acidification/881

3. GLOBAL STATUS AND FUTURE TRENDS OF OCEAN ACIDIFICATION

3.1 Variability

Values for pH and other components of the marine carbon system not only show local and regional natural spatial variability, but can also change temporally, on a diurnal to seasonal basis. Recognition of such variability, and an understanding of its causes, are crucial to the valid interpretation of observational studies and the assessment of anthropogenic ocean acidification trends [1].

The scale of temporal variability can be habitat-specific [2] (Figure 3.1), whilst strong spatial variability can occur both horizontally and vertically in shelf seas (Figure 3.2). It is therefore potentially simpler to detect an ocean acidification signal in the open ocean than in more variable coastal systems [1,3-5]. At many coastal ocean sites, short-term natural variability experienced by benthic organisms has a greater range than the projected pH decline over the next century due to anthropogenic CO_2 emissions [3,6]. For example, the natural variability in ocean pH experienced by warm-water corals can range between pH 6.5 – 8 [7].

Key Messages: Chapter 3

1. Substantial natural temporal and spatial variability occurs in seawater pH, particularly in coastal waters, due to physical, geochemical and biological processes

2. Polar oceans are expected to experience the impacts of ocean acidification sooner than temperate or tropical regions, as their saturation horizons are already shallower than at lower latitudes.

The following physical, geochemical and biological factors may contribute to natural pH variability, particularly in shelf and coastal seas:

- A range of mesoscale hydrodynamic features, including wind-driven upwelling, bringing low pH water to the surface [8]; tidal down-welling [9]; seasonal sea-ice, affecting CO_2 drawdown; and localised temperature gradients (due to frontal features and stratification) that directly affect CO_2 solubility, hence pH and other ocean acidification parameters.
- The biological processes of photosynthesis and respiration/decomposition take up and release CO_2 respectively; both processes vary with depth, and are generally of greater magnitude and more variable in shallow seas than the open ocean. Changes affecting pH occur over day-night cycles and seasonally [5,10]; also locally, due to variable nutrient supply and biological interactions that may promote patchiness of planktonic communities.
- Land and seafloor boundary conditions, and riverine influences, can differ markedly over relatively short distances; all can provide distinct, geologically-derived carbon signatures. River nutrient inputs, affected by land use and sewage-derived pollution, can also serve to enhance biological production (eutrophication). At some coastal sites (and also at tectonically-active deep-sea locations), vents of CO_2 or methane can cause dramatic local pH reductions.
- Atmospheric inputs of nitrogen and sulphur compounds produced by fossil fuel burning and agriculture may also influence pH and carbon chemistry close to source regions [11]

Such dynamic ‘background’ conditions could mean that organisms from coastal waters and shelf seas are less susceptible to future ocean acidification than those from the open ocean, as the former may already be adapted to tolerate low pH. But it could also mean that shallow sea organisms might be exposed to harmful pH thresholds more quickly. In either case, annual mean values for pH or carbonate saturation are likely to be poor predictors of impacts; instead minimum pH levels and/or potential interactions with other stress conditions, including local pollution [12] could be more important.

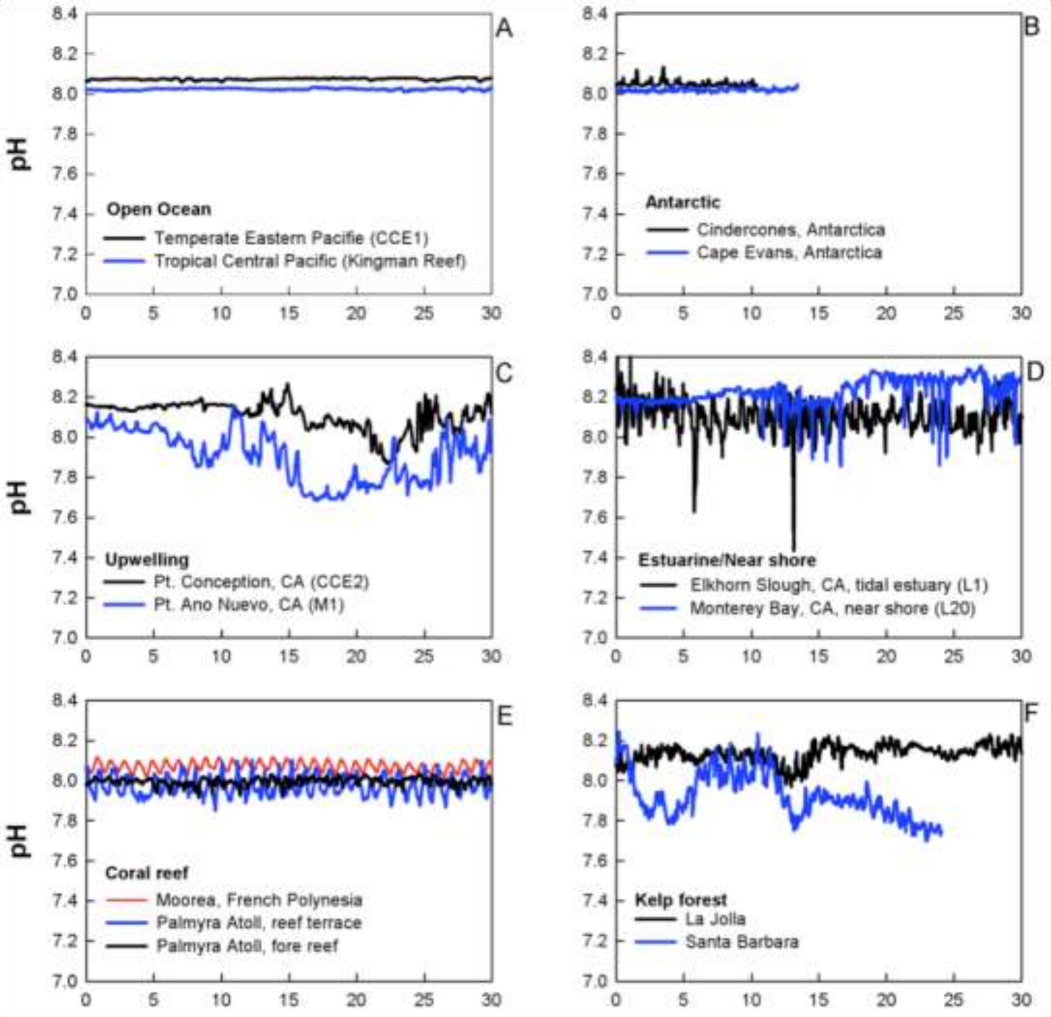


Figure 3.1. Observed temporal variability in pH at 13 locations in the Pacific and Southern Ocean, each over a period of 10-30 days, at 0–15 m water depth [2]. X-axis denotes measurement days.

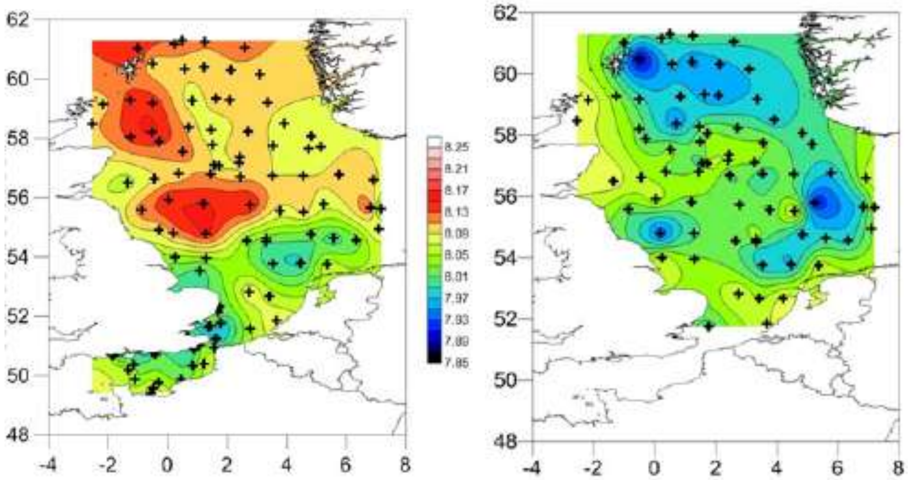


Figure 3.2. Spatial variability in pH in surface (left) and bottom water (right), derived from total alkalinity and dissolved inorganic carbon data for the North Sea in July-August 2011[13]. Many, but not all, of these observed features have been successfully simulated in high-resolution models of the carbon system in the north-west European shelf [14,15]

Several national and international programmes are now working to provide high-quality, standardised observations to provide key knowledge of carbon system changes in the marine environment, hence improving our understanding of present-day variability - and our ability to make reliable projections of future conditions. Global, quality-assured datasets of inorganic carbon, total alkalinity and pCO_2 have now been built through the Global Ocean Data Analysis Project (GLODAP)[16], CARbon in the Atlantic Ocean (CARINA) [17], the Surface Carbon CO_2 Atlas (SOCAT) [18], and the Global Ocean Acidification Observing Network (GOA-ON). Additional details on these initiatives in the context of monitoring ocean acidification are given in Section 3.3 below.

3.2 Modelled simulations of future ocean acidification

Future changes in ocean carbon chemistry will necessarily be very closely linked to future increases in atmospheric CO_2 [19-22][23], with those increases being emission-dependent (Box 3.1). Thus under the lowest current IPCC emission scenario (RCP 2.6), the projected reduction in global mean surface pH by 2100 would be limited to ~0.1 units; under the highest emission scenario (RCP 8.5, the current trajectory), the mean surface pH reduction this century would be at least 0.3 units (Figure 3.3) [22-25]. Those lower and higher pH changes represent further increases in H+ concentrations of around 25% and 170% respectively, in addition to the increase of around 25% that has already occurred since the industrial revolution. The future surface pH change will not be globally-uniform but will vary regionally (Figure 3.4), due to latitudinal differences in temperature and future warming, affecting CO_2 solubility, and basin-scale (and more local) circulation patterns and their future changes.

Box 3.1 IPCC scenarios for future CO_2 emissions

1. Main scenarios used by the Intergovernmental Panel on Climate Change (IPCC) for its 4th Assessment Report (AR4), [IPCC, 2007). These illustrative ‘families’ of pathways were developed in the IPCC Special Report on Emission Scenarios (SRES) [IPCC, 2000], and are referred to in many ocean acidification modelling papers published pre-2012.

A1 – Integrated world, rapid economic growth, limited population growth. Three versions: A1FI (fossil fuel intensive); A1B (balanced) and A1T (non-fossil energy sources).

A2 – Divided world, regional economic growth and continuous population growth (highest emissions in 2100)

B1 – Integrated world, rapid economic growth, limited population growth with global movement towards economic, social and environmental stability (lowest emissions in 2100)

B2 - Divided world, regional economic growth, continuous population growth with regional movement towards economic, social and environmental stability.

2. Main scenarios used by IPCC for its 5th Assessment Report (AR5) [IPCC, 2013], as ‘Representative Concentration Pathways’ (RCPs) [26].

RCP2.6 – lowest emissions, atmospheric CO_2 peaks at ~443 ppm in 2050 before declining to ~421 ppm by 2100. Assumes unspecified ‘negative emissions’ i.e. active CO_2 removal from the atmosphere.

RCP 4.5 – low emissions; atmospheric CO_2 concentrations reach ~538 ppm by 2100

RCP 6.0 – moderate emissions; atmospheric CO_2 concentrations reach ~670 ppm by 2100

RCP 8.5 – high emissions; atmospheric CO_2 concentrations reach ~936 ppm by 2100. Current emissions trend, hence outcome if no substantive mitigation action is taken (“business as usual”).

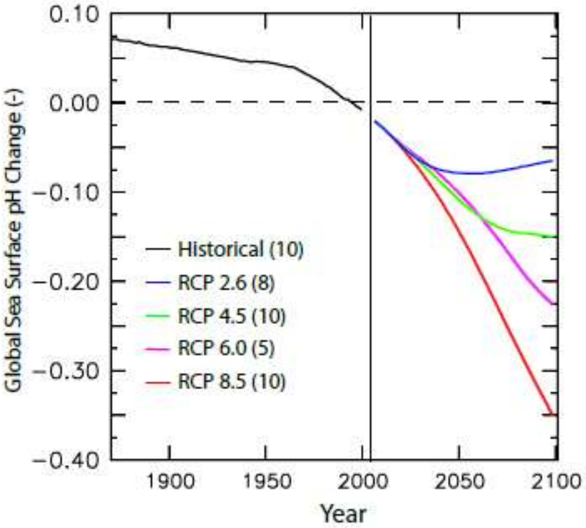


Figure 3.3. Historical and projected changes in global surface ocean pH over 1870-2100 for the four IPCC AR5 scenarios (see Box 3.1). Model means from the Climate Model Intercomparison Project. From [23].

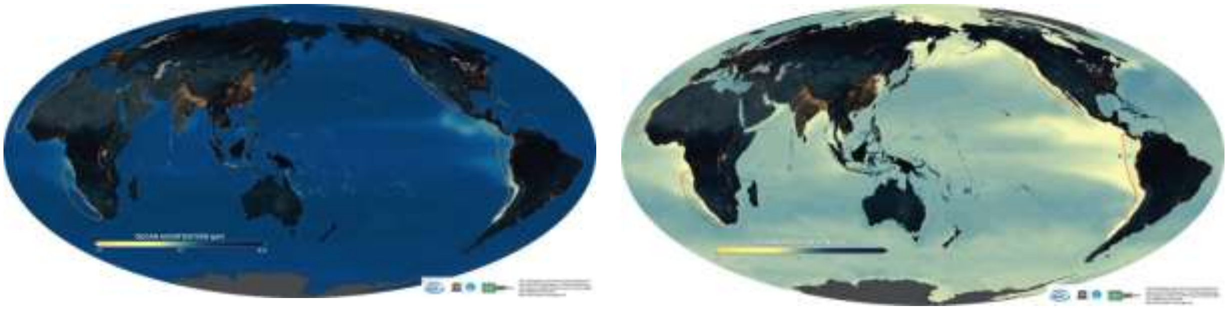


Figure 3.4. Model-derived maps of historical (1850, left) and projected (2100, right) ocean surface pH, with the latter based on the IPCC RCP 8.5 emissions trajectory. From [27]

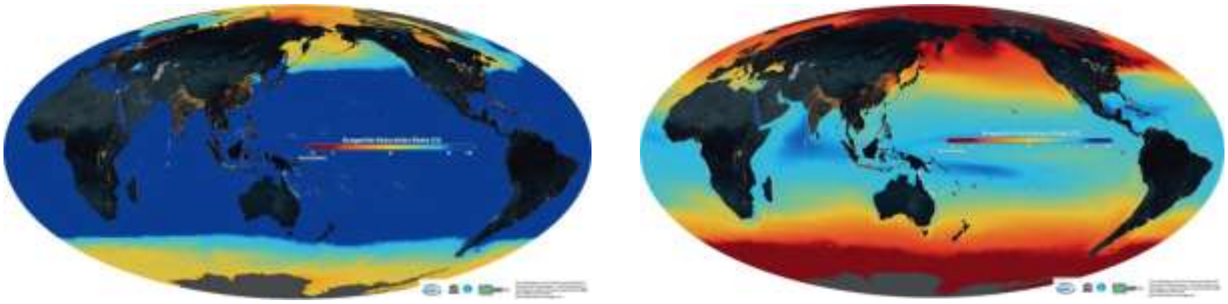


Figure 3.5. Model-derived derived maps of historical (1850, left) and projected (2100, right) aragonite saturation state, with the latter based on the IPCC RCP 8.5 emissions trajectory. From [27]

The aragonite saturation horizon, below which aragonite, the more soluble form of calcium carbonate dissolves, is projected to rise from a few thousand meters to just a few hundred metres in many temperate and tropical oceans by 2100 [24]. As a result of temperature effects on carbon chemistry, high latitude (polar) areas will experience larger declines in surface pH for any given addition of CO_2 from the atmosphere. In Southern Ocean surface water, an atmospheric concentration of about 450 ppm is sufficient for large areas of this region to be under-saturated with respect to aragonite [28]. Similarly, much of the surface Arctic Ocean is projected to become under-saturated for aragonite throughout the year by the middle of the century under most scenarios [21,23] (Figure 3.5).

The seasonally-variable presence of sea-ice in polar regions, and its near-certain future decrease, is an additional confounding influence that is not currently well-represented in projections of future ocean acidification. Sea-ice can significantly affect pH and other components of the carbon system in many ways, including the following:

- Under conditions of offshore transport of sea-ice, the processes of freezing and melting may be spatially separated, that can result in a net transport of inorganic carbon to the deep ocean [29].
- Projected future reductions in sea-ice cover will increase the area of ocean exposed to the atmosphere, enhancing air-sea CO_2 exchange. When coupled with the likely freshening of the surface water (due to melt of land-derived ice) that will accelerate pH decrease in the upper ocean [30].
- Seasonal sea-ice melt can locally enhance stratification and primary production, with indirect effects on pH and other carbon chemistry parameters.

To quantify the importance of such factors, high-resolution ocean carbon models are being developed for high latitude regions, with current emphasis on the Arctic. These models include improved representations of climate-driven changes in ice cover, freshwater inputs, topographically-influenced circulation and biogeochemical processes. Two such models have been developed in association with the Arctic Monitoring and Assessment Programme (AMAP): a 1-D simulation of carbon transformations and fluxes at an Arctic shelf sea site subject to seasonal sea-ice cover and strong riverine influence (Figure 3.6) [31,32], and a regional model for the Atlantic-Arctic gateway region, between Greenland, Svalbard and Norway [30]. An additional uncertainty for the Arctic relates to the potential release of methane, and its subsequent oxidation to CO_2: locally, this could cause a further pH reduction of up to 0.25 units by 2100 [33]

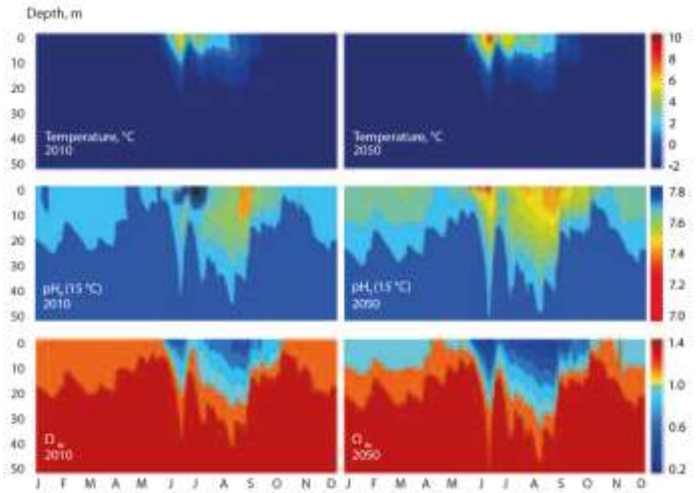


Figure 3.6. Modelled seasonal changes (January to December) in temperature (upper), pH (middle) and aragonite saturation state (lower) for 2010 and projected for 2050 under IPCC SRES B1 for a site at 50m water depth in the Siberian Arctic shelf (Central Laptev Sea). Note that pH mostly increases with water depth (unlike the situation in temperate shelf seas, Fig. 3.2, and the open ocean, Fig. 3.6) and undersaturation is projected to extend from summer-only to year-round within 40 years under a low emissions scenario. From [30]

An important factor to recognize is the longevity of ocean acidification: long after carbon emissions are curtailed, ocean acidification will remain. Anthropogenic increases in atmospheric CO_2 and perturbations to ocean chemistry will take tens to hundreds of thousands of years to return to pre-industrial values [34], as CO_2 will be slowly buffered by the dissolution of calcium carbonate sediments and the weathering of silicates to promote the return of carbon back into geological reservoirs.

3.3 Current status of global observations

Observations of ocean acidification are not yet on a fully global scale, not only because of the relatively short time of awareness of the importance of such changes, but also due to the high cost of research expeditions; the inaccessibility of many regions; the relative unavailability of highly accurate and reliable pH sensors; and the current limitations of autonomous monitoring techniques. There is also need to collect data on other environmental variables for valid interpretation. Nevertheless, long time series do exist on the changing marine carbon system in the central Pacific (Hawaii Ocean Time series, HOT) and North Atlantic (Bermuda Atlantic Time-series Study, BATS; European Station for Time-series in the Ocean, ESTOC), quantifying surface pH decline over the last several decades (over the range -0.0016 to -0.0019 yr^{-1}) [35-37]. The observed decline in surface pH at these three open-ocean stations is consistent with a surface ocean that is closely tracking the increase in atmospheric CO_2 levels over the past three decades [38].

Synthesis products on observations of ocean pCO_2 and air-sea CO_2 fluxes have been developed by the Global Ocean Data Analysis Project (GLODAP)[16], CARbon in the Atlantic Ocean (CARINA) [17], the Surface Carbon CO_2 Atlas (SOCAT) [18], and PACIFICA [39]. These initiatives include analyses of the penetration of anthropogenic carbon to the ocean interior, due to entrainment, mixing, and deep-water formation. In the North Atlantic and Southern Ocean, signals of decreasing pH have already been observed at the ocean floor [40-43]. Such changes involve more than a simple shoaling of aragonite and calcite saturation horizons, since the zone of low pH water may be extending downwards as well as upwards (Figure 3.7). In the Pacific and the South Atlantic, signals of anthropogenic carbon have also been observed in intermediate waters [44,45]. For all ocean basins, model projections indicate that ocean acidification will occur throughout the water column by 2100.

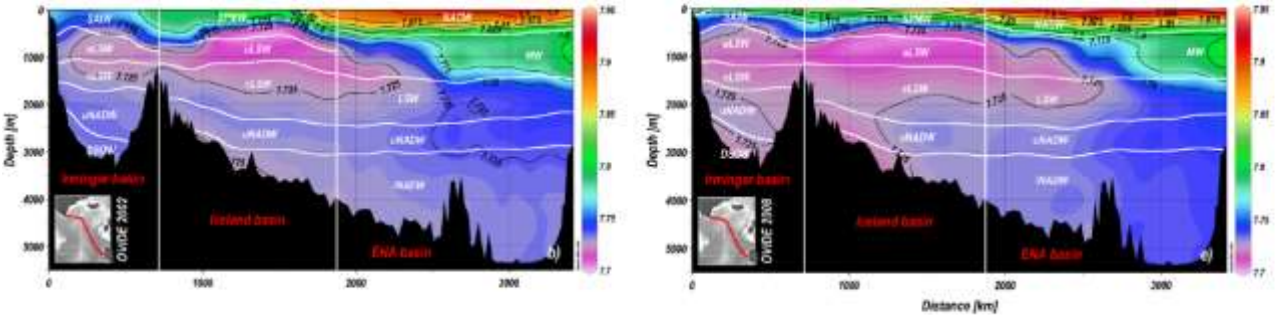


Figure 3.7. Measured pH profiles in the north-east Atlantic along a 3,400 km transect from SE Greenland to Portugal in 2002 (left) and 2008 (right). Transect data also collected in 1993, 2002 and 2006, fully consistent with this rapid expansion in the volume of low-pH intermediate water, and associated changes in seafloor conditions. From [40].

Recent international effort has been directed at extending and complementing these existing programmes to more explicitly address ocean acidification and its impacts, with increased attention to shelf seas and coastal regions. Relevant activities are being initiated and implemented through the newly-established Global Ocean Acidification Observing Network (GOA-ON) (Figure 3.8). GOA-ON aims to provide an understanding of ocean acidification conditions and the ecosystem response, also to deliver the data needed to optimize ocean acidification modelling. Since the potential scope for biological observing is extremely wide, GOA-ON will build on, and work in close liaison with, the Global Ocean Observing System (GOOS) and its Framework for Ocean Observation. Other bodies contributing to the development of the network include the IAEA Ocean Acidification International Coordination Centre (OA-ICC), IOC-UNESCO, the International Ocean Carbon Coordination Project (IOCCP), and a range of national funding agencies. To date, most ocean acidification observations have been ship-based. However, increasing use is expected to be made of pH sensors on profiling floats [46] and using underwater gliders; such issues are also considered in Section 6.

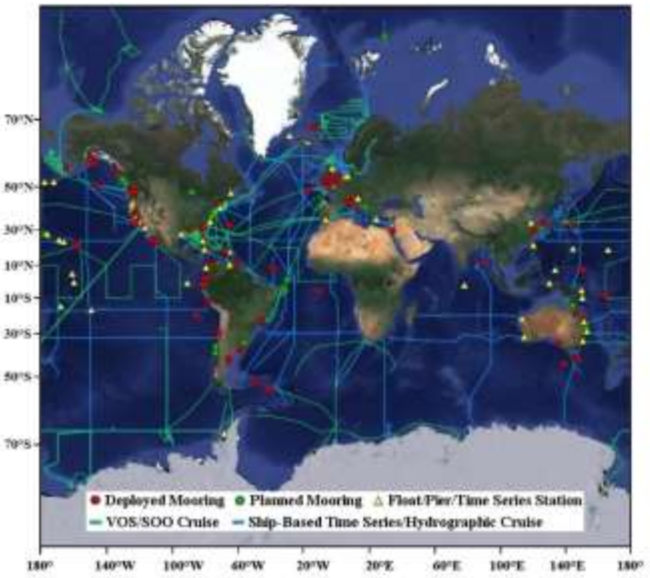


Figure 3.8. Components of the developing Global Ocean Acidification Observing Network (GOA-ON), including moorings, time series stations, and ship-based surveys, by voluntary observing ships (VOS), ships of opportunity (SOO) and research vessels. Status at December 2013, from draft GOA-ON Requirements and Governance Plan [47].

1. Friedrich T, Timmermann A, Abe-Ouchi A, Bates NR, Chikamoto MO, et al. (2012) Detecting regional anthropogenic trends in ocean acidification against natural variability. Nature Climate Change 2: 167-171.
2. Hofmann GE, Smith JE, Johnson KS, Send U, Levin LA, et al. (2011) High-Frequency Dynamics of Ocean pH: A Multi-Ecosystem Comparison. Plos One 6.
3. Duarte CM, Hendriks IE, Moore TS, Olsen YS, Steckbauer A, et al. (2013) Is Ocean Acidification an Open-Ocean Syndrome? Understanding Anthropogenic Impacts on Seawater pH. Estuaries and Coasts 36: 221-236.
4. Provoost P, Van Heuven S (2010) Long-term record of pH in the Dutch coastal zone: a major role for eutrophication-induced changes. Biogeosciences 7: 4127-4152.
5. Johnson ZI, Wheeler BJ, Blinebry SK, Carlson CM, Ward CS, et al. (2013) Dramatic Variability of the Carbonate System at a Temperate Coastal Ocean Site (Beaufort, North Carolina, USA) Is Regulated by Physical and Biogeochemical Processes on Multiple Timescales. Plos One 8.
6. Wootton JT, Pfister CA (2012) Carbon System Measurements and Potential Climatic Drivers at a Site of Rapidly Declining Ocean pH. Plos One 7.
7. Shaw EC, McNeil BI, Tilbrook B, Matear R, Bates ML (2013) Anthropogenic changes to seawater buffer capacity combined with natural reef metabolism induce extreme future coral reef CO2 conditions. Global Change Biology 19: 1632-1641.
8. Feely RA, Sabine CL, Hernandez-Ayon JM, Ianson D, Hales B (2008) Evidence for upwelling of corrosive "acidified" water onto the continental shelf. Science 320: 1490-1492.
9. Findlay HS, Artioli Y, Navas JM, Hennige SJ, Wicks LC, et al. (2013) Tidal downwelling and implications for the carbon biogeochemistry of cold-water corals in relation to future ocean acidification and warming. Global Change Biology 19: 2708-2719.
10. Zhai W-D, Zheng N, Huo C, Xu Y, Zhao H-D, et al. (2014) Subsurface pH and carbonate saturation state of aragonite on the Chinese side of the North Yellow Sea: seasonal variations and controls. Biogeosciences 11: 1103-1123.
11. Doney SC, Mahowald N, Lima I, Feely RA, Mackenzie FT, et al. (2007) Impact of anthropogenic atmospheric nitrogen and sulfur deposition on ocean acidification and the inorganic carbon system. Proceedings of the National Academy of Sciences of the United States of America 104: 14580-14585.
12. Roberts DA, Birchenough SNR, Lewis C, Sanders MB, Bolam T, et al. (2013) Ocean acidification increases the toxicity of contaminated sediments. Global Change Biology 19: 340-351.
13. Greenwood N, Pearce D (2013) Impacts of Ocean Acidification. In: Williamson P, Turley CM, Brownlee C, Findlay HS, Ridgwell A et al., editors. MCIP Science Review. pp. 34-48.
14. Artioli Y, Blackford J, Butenschon M, Holt JT, Wakelin SL, et al. (2012) The carbonate system of the NW European shelf: sensitivity and model validation. Journal of Marine Systems 102-104: 1-13.
15. Artioli Y, Blackford J, Nondal G, Bellerby RGJ, Wakelin SL, et al. (2014) Heterogeneity of impacts of high CO2 on the North Western European Shelf. Biogeosciences 11: 601-612.
16. Key RM, Kozyr A, Sabine CL, Lee K, Wanninkhof R, et al. (2004) A global ocean carbon climatology: Results from Global Data Analysis Project (GLODAP). Global Biogeochemical Cycles 18.
17. Key RM, Tanhua T, Olsen A, Hoppema M, Jutterstrom S, et al. (2010) The CARINA data synthesis project: introduction and overview. Earth Systems Science Data 2: 105-121.
18. Bakker D.C.E. and 80 others. 2014. An update to the Surface Ocean CO_2 Atlas (SOCAT version 2). Earth System Science Data, 6, 69-90; doi: 10.5194/essd-6-69-2014
19. Zeebe RE (2012) History of Seawater Carbonate Chemistry, Atmospheric CO_2, and Ocean Acidification. Annual Review of Earth and Planetary Sciences, Vol 40 40: 141-165.
20. Caldeira K, Wickett ME (2005) Ocean model predictions of chemistry changes from carbon dioxide emissions to the atmosphere and ocean. Journal of Geophysical Research-Oceans 110.

21. Steinacher M, Joos F, Froelicher TL, Plattner GK, Doney SC (2009) Imminent ocean acidification in the Arctic projected with the NCAR global coupled carbon cycle-climate model. Biogeosciences 6: 515-533.
22. Denman K, Christian JR, Steiner N, Poertner H-O, Nojiri Y (2011) Potential impacts of future ocean acidification on marine ecosystems and fisheries: current knowledge and recommendations for future research. Ices Journal of Marine Science 68: 1019-1029.
23. Bopp L, Resplandy L, Orr JC, Doney SC, Dunne JP, et al. (2013) Multiple stressors of ocean ecosystems in the 21st century: projections with CMIP5 models. Biogeosciences 10: 6225-6245.
24. Orr JC, Fabry VJ, Aumont O, Bopp L, Doney SC, et al. (2005) Anthropogenic ocean acidification over the twenty-first century and its impact on calcifying organisms. Nature 437: 681-686.
25. McNeil BI, Matear RJ (2007) Climate change feedbacks on future oceanic acidification. Tellus Series B-Chemical and Physical Meteorology 59: 191-198.
26. Moss RH, Edmonds JA, Hibbard KA, Manning MR, Rose SK, et al. (2010) The next generation of scenarios for climate change research and assessment. Nature 463: 747-756.
27. IGBP, IOC, SCOR (2013). Ocean Acidification Summary for Policymakers 2013. International Geosphere-Biosphere Programme. Stockholm, Sweden.
28. McNeil B, Matear R (2008) Southern Ocean acidification: A tipping point at 450-ppm atmospheric CO2. Proceedings of the National Academy of Science 105: 18860-18864.
29. Loose B, Schlosser P (2011) Sea ice and its effect on CO2 flux between the atmosphere and the Southern Ocean interior. Journal of Geophysical Research-Oceans 116.
30. Bellerby RGJ, Miller L, Croot P, Anderson L, Azetsu-Scott K, et al. (2013) Acidification of the Arctic Ocean. Arctic Ocean Acidification Assessment, Arctic Monitoring and Assessment Programme (AMAP). Oslo.
31. Wahlstrom I, Omstedt A, Bjork G, Anderson LG (2013) Modeling the CO2 dynamics in the Laptev Sea, Arctic Ocean: Part II. Sensitivity of fluxes to changes in the forcing. Journal of Marine Systems 111: 1-10.
32. Wahlstrom I, Omstedt A, Bjork G, Anderson LG (2012) Modelling the CO2 dynamics in the Laptev Sea, Arctic Ocean: Part I. Journal of Marine Systems 102: 29-38.
33. Biastoch A, Treude T, Rüpke LH, Riebesell U, Roth C, et al. (2011) Rising Arctic Ocean temperatures cause gas hydrate destabilization and ocean acidification. Geophysical Research Letters 38: n/a-n/a.
34. Archer D (2005) Fate of fossil fuel CO2 in geologic time. Journal of Geophysical Research-Oceans 110.
35. Dore JE, Lukas R, Sadler DW, Church MJ, Karl DM (2009) Physical and biogeochemical modulation of ocean acidification in the central North Pacific. Proceedings of the National Academy of Sciences of the United States of America 106: 12235-12240.
36. Bates NR, Best MHP, Neely K, Garley R, Dickson AG, et al. (2012) Detecting anthropogenic carbon dioxide uptake and ocean acidification in the North Atlantic Ocean. Biogeosciences 9: 2509-2522.
37. Santana-Casiano JM, Gonzalez-Davila M, Rueda M-J, Llinas O, Gonzalez-Davila E-F (2007) The interannual variability of oceanic CO2 parameters in the northeast Atlantic subtropical gyre at the ESTOC site. Global Biogeochemical Cycles 21.
38. IPCC (2013) Twelfth Session of Working Group I, Summary for Policymakers.
39. Suzuki T. and 18 others. (2013) PACIFICA Data Synthesis Project. ORNL/CDIAC-159, NDP-092. Carbon Dioxide Information Analysis Center, Oak Ridge TN, USA; doi: 10.3334/CDIOAC/OTG.PACIFICA_NDP092.
40. Vazquez-Rodriguez M, Perez FF, Velo A, Rios AF, Mercier H (2012) Observed acidification trends in North Atlantic water masses. Biogeosciences 9: 5217-5230.
41. Vazquez-Rodriguez M, Touratier F, Lo Monaco C, Waugh DW, Padin XA, et al. (2009) Anthropogenic carbon distributions in the Atlantic Ocean: data-based estimates from the Arctic to the Antarctic. Biogeosciences 6: 439-451.
42. Hauck J, Hoppema M, Bellerby RGJ, Voelker C, Wolf-Gladrow D (2010) Data-based estimation of anthropogenic carbon and acidification in the Weddell Sea on a decadal timescale. Journal of Geophysical Research-Oceans 115.
43. Olafsson J, Olafsdottir SR, Benoit-Cattin A, Danielsen M, Arnarson TS, et al. (2009) Rate of Iceland Sea acidification from time series measurements. Biogeosciences 6: 2661-2668.
44. Byrne RH, Mecking S, Feely RA, Liu X (2010) Direct observations of basin-wide acidification of the North Pacific Ocean. Geophysical Research Letters 37.
45. Resplandy L, Bopp L, Orr JC, Dunne JP (2013) Role of mode and intermediate waters in future ocean acidification: Analysis of CMIP5 models. Geophysical Research Letters 40: 3091-3095.
46. http://www.mbari.org/chemsensor/floatviz.htm
47. GOA-ON http://www.pmel.noaa.gov/co2/GOA-ON/

4. WHAT THE PAST CAN TELL US – PALEO-OCEANOGRAPHIC RESEARCH

As well as using models to project climate change, we can better understand the future impacts of ocean acidification by studying how biogeochemical cycles operated in the past, and the impact past events had on marine ecosystems.

In addition to variations in seawater acidity from place to place because of circulation patterns, biological activity, and other oceanographic processes (see previous section), the average state of the ocean can also change through time in response to natural variations in the global carbon cycle. Past changes in ocean acidity can be studied by chemical analysis of the skeletons of dead organisms such as molluscs, foraminifera, corals and algae, or of ocean sediments which are accessible by drilling into the sea-bed. Deep-sea cores commonly contain abundant fossils of calcifying (carbonate producing) plankton such as foraminifera and coccolithophores (Figure 4.1), which are among the groups considered most at risk in future ocean acidification.

The paleo-record can be used to extend the current record of acidity changes as it stretches back millions of years in time. Over the longer term, it contains evidence of: (1) cyclic changes in ocean chemistry associated with glacial / interglacial cycles with sometimes abrupt transitions; (2) multi-million year trends related to global tectonics; and, perhaps of most interest, (3) past sudden events of similar scale (if not rate) to the current human-induced change to the carbon cycle. These abrupt events provide us with real-world examples of profound environmental changes that allow us to study the past long-term response of marine organisms to ocean acidification including, for example, their extinction, migration, assemblage changes, and changes in calcification style. This information from the past can be compared with the results of modern field and laboratory research.

Key Messages: Chapter 4

1. During ocean acidification which occurred ~56 million years ago over a period of ~6000 years, a significant number of deep-sea calcifying organisms became extinct

2. Current ocean acidification is projected to reach similar levels over 500 years

3. Ocean acidification may have been a contributing factor to four out of five coral reef crises in the last 500 million years

4. The paleo-record confirms that ocean acidification takes thousands of years to return to original levels following a CO_2 input event

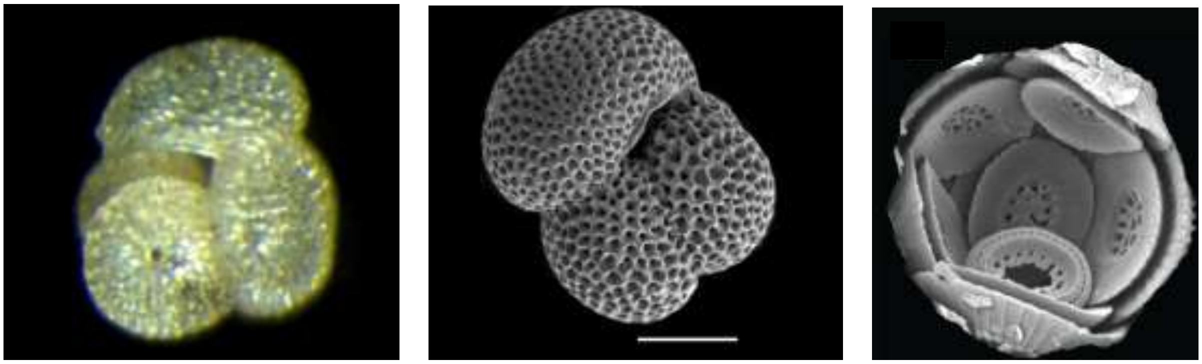


Figure 4.1. A light microscope and scanning electron microscope image of planktonic foraminifera specimens from Paleocene-Eocene Thermal Maximum (PETM, ~56 million years ago) sediments from Tanzania. Geochemical analysis of foraminifera shells can provide information about oceanic chemistry millions of years ago. Scale bar 100 µm. The far right panel is a well preserved coccosphere. Source: P. Pearson (foraminifera), P. Bown (coccosphere).

4.1 Reconstructing past ocean acidification events

To understand the rate and magnitude of past carbon cycle perturbations and their effect on seawater pH it is necessary to generate data of various sorts to help constrain geochemical models. One approach is the study of calcium carbonate content of deep-sea sediments deposited at different water depths. Another valuable tool is to measure the boron isotopic composition ($\delta^{11}B$) of marine carbonates which is influenced by the pH of the water from which it was precipitated. Trace element to calcium ratios of carbonates and the carbon isotope ratio ($\delta^{13}C$) can also help identify changes in the global carbon cycle.

4.2 The Paleocene-Eocene Thermal Maximum – A natural past ‘experiment’ in ocean acidification

The Paleogene (~33-65 million years ago) was a period of elevated global temperatures with high levels of atmospheric CO_2 that at times exceeded 1000 ppm [1]. It was punctuated by a series of “hyperthermals”, which are geologically short-lived warming events characterised by evidence of acidification of the oceans [1]. The largest of these was the Paleocene-Eocene Thermal Maximum (PETM) ~56 million years ago [2] which has been proposed as the closest geological analogue to modern day ocean acidification due to the volume of carbon released [3]. During this period ~2000-3000 petagrams (also known as gigatonnes) of carbon was released into the Earth’s atmosphere over thousands of years[4,5] and global temperatures increased by about 5°C [6]. Coincident with this climatic shift was a lowering of oceanic pH, as evidenced by dissolution of carbonate at the seafloor [7] (Figure 4.2).

Figure 4.2. Atlantic Ocean deep-sea core from the Integrated Ocean Drilling Program. Note the brown section of the core that represents the dissolution of deep-sea carbonate at the Paleocene-Eocene boundary. This could represent a lack of calcifiers during that time period or the dissolution of dead shells. Source: James Zachos.

4.3 The impact of past ocean acidification upon calcifiers

Good geological records can be collected of corals and calcifying plankton due to their structure and their settlement respectively. Understanding the geological history of coral reefs, and whether past coral reef 'crises' were initiated by ocean acidification is of great importance as we consider the future fate of coral reefs. Kiessling and Simpson (Table 4.1) [8] investigated whether 1) reef crises (declines in carbonate production) and 2) reef mass extinctions were contributed to ocean acidification, and concluded that it was likely that most of the reef crises in the last 500 million years were partially governed by ocean acidification and rapid global warming (Table 4.1).

Table 4.1. Summary of results from Kiessling and Simpson [8], and assessment of ocean acidification as a probable cause. Biotic changes include impacts on physiologically buffered and unbuffered organisms.

Time	Reef crisis	Biotic change	Evidence for OA*
Late Ordovician (445.6-443.7 Ma)	Not evident	Mass depletion of biodiversity during double mass extinction. Unselective with respect to buffering	None
Late Devonian (374.5 Ma)	Mostly metazoan (especially for corals and sponges)	Mass depletion of biodiversity. Selective extinction of corals and sponges over prolonged period of time	Weak
Middle - Late Permian (260.4 Ma)	Coral-sponge reef crisis only	Substantial extinction, weakly selective with respect to buffering	None
Permian - Triassic (251 Ma)	Massive for all reef types	Mass depletion of biodiversity and mass extinction, especially for unbuffered organisms	Strong
Triassic – Jurassic (199.6 Ma)	Massive for all reef types	Mass depletion of biodiversity and mass extinction selective against corals, sponges, and unbuffered organisms	Strong
Early Jurassic (183 Ma)	Coral reef crisis	Modest but selective extinction of corals and other unbuffered organisms	Strong
Cretaceous – Paleogene (65.5 Ma)	Not evident	Mass depletion of biodiversity and mass extinction, selective against buffered organisms	Weak
Paleocene – Eocene (55.8 Ma)	Coral reef crisis	Background extinction, except for benthic foraminifers	Strong

*OA=ocean acidification

However, this does not reflect the full story of coral history, and to fully understand the geological history of coral reefs, it seems likely a combined environment and evolutionary approach may be needed. Indeed, the modern Scleractinia (the framework forming corals as we know them today) appeared in the middle Triassic period, and two main orders of coral, the Rugosa and the Tabulata, became extinct before this at the end of the Permian period. These corals were believed to be calcitic, and not aragonitic like the vast majority of today's corals. This period was clearly characterized as a time of environmental perturbations with unusual seawater chemistry [9,10], and thus the 'Sandburg curve' [11] which details the dominance of calcitic and aragonitic biomineralisation strategies by marine organisms through time may be an important component of future historical coral research with respect to changing climates.

It appears that not all groups of organisms with exposed skeletal structures were affected by ocean acidification in the same way over the last 300 million years. Some climate and ocean acidification events are associated with widespread extinction, whereas others are characterized by evolutionary turnover [3]. For example, during the PETM both planktonic foraminifera and coccolithophore communities demonstrated significant range shifts but they were not subject to mass extinction. Tropical communities migrated to higher latitudes, coincident with the appearance of short-lived “excursion taxa” that appear in the fossil record in lower latitude assemblages [6]. In contrast, there was a severe extinction of deep-sea benthic foraminifera with up to 50% of species lost from the fossil record [12]. The extinction saw the disappearance of long-lived Paleocene species and the post extinction taxa were commonly smaller and had thinner shells [12].

Recent research has provided detailed information on biomineralisation of the skeletons of pelagic organisms that are likely sensitive to changes in surface water chemistry. Analysis of the architecture of coccolithophores has distinguished impacts on the skeleton that are associated with cellular function versus those associated with external carbonate chemistry of the water they experienced during the PETM [13]. Currently, observed changes suggest that the impact of ocean acidification across the PETM was relatively low compared to biogeographic range changes driven by warming and changes in circulation and the hydrologic cycle.

This does not mean we should not be concerned for calcifiers under our current climate regime. Clearly, communities responded significantly to the combined environmental impacts of the PETM, which like today, consisted of ocean acidification with additional environmental changes associated with increased CO_2, such as changes in temperature and oxygenation [14]. This is particularly the case for organisms that are unable to migrate in order to avoid environmental change, such as longer lived, sessile organisms like oysters and corals. It is especially important to remember that the changes seen during the PETM took place over many thousands of years, at least 10 times slower than anticipated rates of warming and OA in the century ahead[14]. When the rate of carbon uptake into the ocean outstrips its capacity to absorb it, a reduction in pH goes hand in hand with a lowering of its saturation state [15]. It is this saturation state (buffering capacity) of the ocean that could impact the functioning of many calcifying organisms, such as tropical reef-forming corals and planktonic organisms that form the base of pelagic food webs, especially in the vulnerable Arctic and Antarctic regions [14].

4.4 Using the geological record to inform our understanding of ocean acidification

The geological record provides tangible evidence of the impacts of ocean acidification on environments and ecosystems, and provides a unique long-term perspective. However distinguishing the effects of acidification from associated environmental variables in the past is difficult and there is no perfect geological analogue for modern day ocean acidification. The PETM, in particular, is widely studied because it is comparable in magnitude to predicted anthropogenic CO_2 release, but it differs markedly in terms of rate of change as it occurred over thousands rather than tens or hundreds of years as it the case today. Even so it provides an invaluable test-bed for studying the overall impact and subsequent recovery of the earth system and biotic communities, and potential biotic sensitivity to abrupt climate change.

4.5 Timescales of ocean acidification

In Earth history, ocean carbonate saturation is generally well regulated by the simple requirement that on ‘long’ (>10 kyr) timescales, sources (weathering) and sinks (shallow- and deep-water $CaCO_3$ burial) are kept in balance and regulated by the position of the calcium carbonate saturation depths. Only events involving geologically ‘rapid’ (<10 kyr) CO_2 release will overwhelm the ability of the ocean and sediments to regulate, producing a coupled decline in both pH and saturation state [15]. The onset of the PETM occurred over a timescale of <10,000 years[16] and released ~2000-3000 petagrams of carbon into the Earth’s atmosphere [17].

Today's climate change projections calculate that ~ 5000 petagrams of carbon will be released into the atmosphere over the next 500 years if we follow a 'business as usual' scenario [18,19]. In Figure 4.4A, carbon released into the atmosphere during the PETM, and projected carbon outputs from human activities have been overlaid to provide perspective on the timescales involved. As a result of the carbon released in 4.4A, the saturation state of calcite (one of the mineral forms of calcium carbonate) decreases (Figure 4.4B). An important point to note is the timescale for the saturation state for calcite to ‘recover’ to previous levels. Following the PETM, this took ~100,000 years [7], and it is projected to take a similar length of time following projected anthropogenic carbon emissions. Thus we can see that ocean acidification is not a short-lived problem, and could take many thousands of years to return to pre-industrial levels even if carbon emissions are curbed.

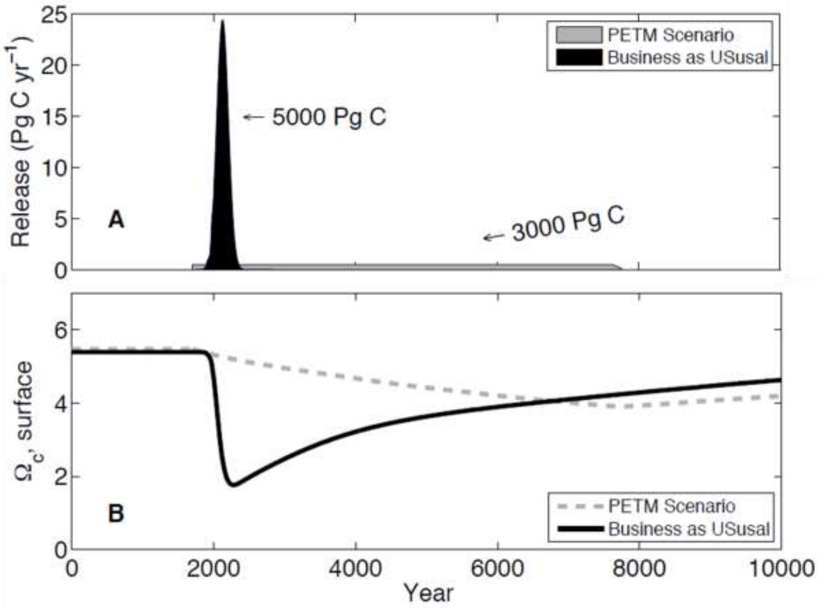


Figure 4.3. Paleocene-Eocene Thermal Maximum (PETM) versus present day time scales.(A) Carbon emission scenarios as projected for the future (5000 petagrams carbon over ~500 years [17,18] and the PETM (3000 petagrams of carbon over ~6000 years). The onset of the PETM has been aligned with the onset of industrialisation. (B) Changes in surface-ocean saturation state of calcite simulated with the Long-term Ocean-atmosphere-Sediment Carbon cycle Reservoir (LOSCAR) Model in response to the carbon input shown in (A). Source: Gattuso and Hansson 2011 [20] © By permission of Oxford University Press.

1. Zachos JC, Dickens GR, Zeebe RE (2008) An early Cenozoic perspective on greenhouse warming and carbon-cycle dynamics. Nature 451: 279-283.
2. Kennett JP, Stott LD (1991) Abrupt deep-sea warming, palaeoceanographic changes and benthic extinctions at the end of the paleocene. Nature 353: 225-229.
3. Hönisch B, Ridgwell A, Schmidt DN, Thomas E, Gibbs SJ, et al. (2012) The geological record of ocean acidification. Science (New York, NY) 335: 1058-1063.
4. Dickens GR (2011) Methane release from gas hydrate systems during the Paleocene-Eocene thermal maximum and other past hyperthermal events: setting appropriate parameters for discussion. Climate of the Past Discussions 7: 1139-1174.
5. Dickens GR (2011) Down the Rabbit Hole: toward appropriate discussion of methane release from gas hydrate systems during the Paleocene-Eocene thermal maximum and other past hyperthermal events. Climate of the Past 7: 831-846.
6. McInerney FA, Wing SL (2011) The Paleocene-Eocene Thermal Maximum: A Perturbation of Carbon Cycle, Climate, and Biosphere with Implications for the Future. In: Jeanloz R, Freeman KH, editors. Annual Review of Earth and Planetary Sciences, Vol 39. pp. 489-516.
7. Zachos JC, Rohl U, Schellenberg SA, Sluijs A, Hodell DA, et al. (2005) Rapid acidification of the ocean during the Paleocene-Eocene thermal maximum. Science 308: 1611-1615.
8. Kiessling W, Simpson C (2011) On the potential for ocean acidification to be a general cause of ancient reef crises. Global Change Biology 17: 56-67.
9. Knoll AH, Bambach RK, Canfield DE, Grotzinger JP (1996) Comparative earth history and Late Permian mass extinction. Science 273: 452-457.
10. Roberts JM, Wheeler A, Freiwald A, Cairns SD (2009) Cold-Water Corals: The Biology and Geology of Deep-Sea Coral Habitats: Cambridge University Press.
11. Sandberg PA (1983) An oscillating trend in Phanerozoic non-skeletal carbonate mineralogy. Nature 305: 19-22.
12. Thomas E (2007) Cenozoic mass extinctions in the deep sea: What perturbs the largest habitat on Earth? Large Ecosystem Perturbations: Causes and Consequences 424: 1-23.
13. Gibbs SJ, Poulton AJ, Bown PR, Daniels CJ, Hopkins J, et al. (2013) Species-specific growth response of coccolithophores to Palaeocene-Eocene environmental change. Nature Geoscience 6: 218-222.
14. Bijma J, Portner HO, Yesson C, Rogers AD (2013) Climate change and the oceans - What does the future hold? Marine Pollution Bulletin 74: 495-505.
15. Ridgwell A, Schmidt DN (2010) Past constraints on the vulnerability of marine calcifiers to massive carbon dioxide release. Nature Geoscience 3: 196-200.
16. Pearson PN, Nicholas CJ (2014) Layering in the Paleocenr/Eocenr boundary of the Milville core is drilling disturbance. PNAS (in press) ; www.pnas.org/cgi/doi/10.1073/pnas.1322077111
17. Diffenbaugh NS, Field CB (2013) Changes in ecologically critical terrestrial climate conditions. Science 341: 486-492.
18. Zeebe RE, Caldeira K (2008) Close mass balance of long-term carbon fluxes from ice-core CO2 and ocean chemistry records. Nature Geoscience 1: 312-315.
19. Zeebe RE, Zachos JC, Caldeira K, Tyrrell T (2008) Carbon emissions and acidification. Science 321: 51-52.
20. Gattuso JP, Hansson L (2011) Ocean Acidification. Oxford: Oxford University Press.

5. IMPACT OF OCEAN ACIDIFICATION ON BIODIVERSITY AND ECOSYSTEM FUNCTION

Ocean acidification will have direct impacts upon a variety of different taxa through different mechanisms such as metabolism, pH regulation, calcification and photosynthesis. These impacts will influence ecosystem dynamics with an end result of potentially altered ecosystem services. Figure 1.3 summarises the interaction between direct effects of CO_2 and pH (non-comprehensive) and ecosystem services; in this Chapter , responses are considered in greater detail.

5.1 Physiological responses

5.1.1 Ocean acidification cellular processes

Most organisms regulate some aspects of their internal (extra- or intracellular) pH, either for calcification purposes, or because their metabolic activity requires some level of regulation. This 'acid-base balance' or regulation is an energetic process, so a disruption caused by changing external CO_2 levels will require energy to maintain aspects of extra – or intracellular balance. Several studies, e.g. on deep sea invertebrates [1] and fish [2,3] indicate that animals at high pCO_2 require more energy as compared to those at low pCO_2, leading to the hypothesis that additional energy is needed to maintain the acid-base balance. This implies that, if a constant total energy budget is assumed, then increasing energetic investment into acid-base regulation will decrease allocation to other functions, such as reproduction or growth (Figure 5.1). Some studies are now demonstrating energetic compensation behaviours [4], but if acid-base balance is not achieved, metabolism can become depressed as a short-term response in order to suppress ATP demand to extend potential tolerance [5]. However, this is not advantageous as it is typically at the expense of processes such as protein synthesis [5-7].

Key Messages: 5.1.1

1. Ocean acidification can lead to acid-base imbalance in many marine organisms such as fish, invertebrates and sediment fauna

2. Acid base imbalance can lead to metabolic suppression, reduced protein synthesis and reduction in long-term fitness

3. Some species can modify energetic allocation to compensate for increased energetic costs of OA

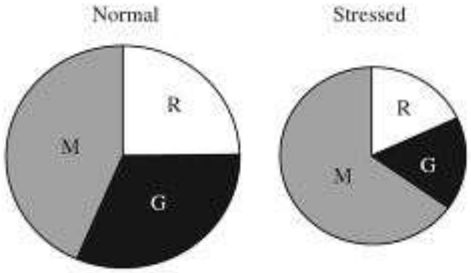


Figure 5.1. Hypothetical energy budget for normal and stressed organisms. M = maintenance costs, R = reproduction and G = growth. In this hypothetical energy budget, if metabolic depression is also induced by ocean acidification, the total energy budget may also decrease (hence the smaller pie on the right). Barry et al. 2011[8] in Gattuso and Hansson [9]. © By permission of Oxford University Press

Many marine organisms produce shells and other structures composed of calcium carbonate ($CaCO_3$). Future ocean acidification will lower the saturation state of calcium carbonate (aragonite and calcite) and if the water is undersaturated, dissolution of unprotected calcium carbonate will occur. The chemistry of that dissolution process is well-established [10,11]. However, the effects on calcium carbonate formation –

biocalcification –- are very much harder to predict. This is because in most organisms biocalcification does not occur directly from seawater but rather in a compartment or space with regulated chemistry and biochemistry, which allows controlled crystal formation. Relevant ions have to be transported into these compartments, and under future ocean acidification scenarios, these transport mechanisms may become slower and less efficient; alternatively, compensation responses may occur. The degree to which different groups of organisms are sensitive to changes in carbonate chemistry has become a major focus of ocean acidification research. Here we give a more in depth explanation in corals, as they are one of the key marine calcifiers that engineer important marine habitats.

In corals, skeletons are laid down in a process controlled by specialized calcifying cells in an extracellular calcifying medium semi-isolated from the surrounding seawater environment [12]. Since the growing skeleton is not in direct contact with seawater, it is not immediately clear why coral calcification should be affected by ocean acidification occurring in the exterior seawater [13]. Recent research on cellular processes associated with calcification has started to identify the pathways that underlie the sensitivity of corals to ocean acidification. Firstly, it has been shown that there is a passage of ions and molecules from exterior seawater to the calcifying fluid [14]. However, the passage of seawater is restrictive and coral tissues protect the skeleton from potential dissolution [15,16]. One way for corals to exert biological control to buffer against the effects of ocean acidification is to increase pH in the calcifying fluid [17], effectively increasing $\Omega_{aragonite}$ at the site of calcification [18,19]. It is thought that this process requires greater investment into acid-base regulation of calcifying cells and fluid under ocean acidification at an energetic cost to the coral [18-21]. Gene expression data in corals show signs that ocean acidification may start to impair the calcification process when coral acid-base and ion regulatory systems struggle to maintain homeostasis in the calcifying cells [21,22].

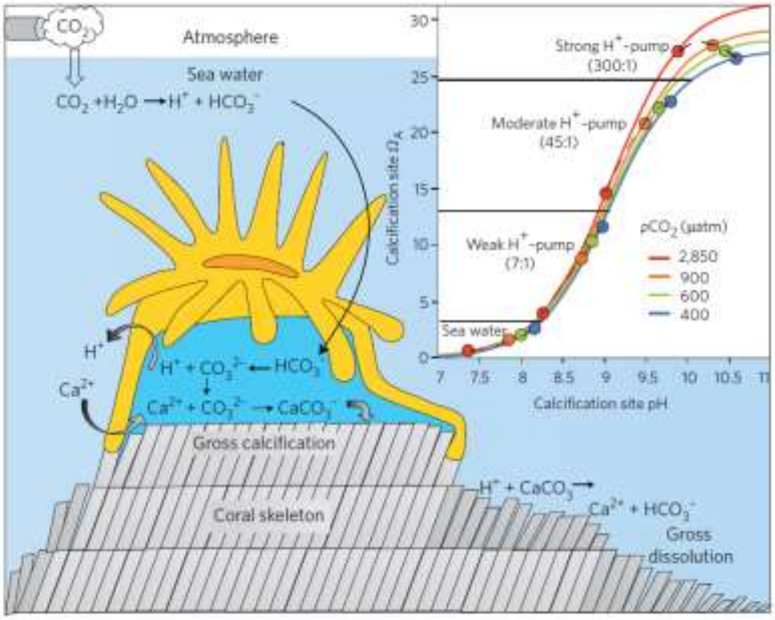


Figure 5.2. Schematic representation of coral calcification and dissolution, showing how saturation state of the calcifying fluid (shaded dark blue; vertically exaggerated) is affected by external pH and the strength of the H^+ pump. The latter might be weak, moderate or strong; for strong H^+-pumping corals, the rate of gross calcification may initially increase under increased CO_2 levels, as shown in the inset graph, while net calcification rates may decline owing to dissolution of exposed skeleton. From [16].

5.1.2 Fertilization, early life and settlement

Many marine invertebrates have "mixed" life-cycles in which different developmental stages inhabit benthic and pelagic environments. The persistence and success of these species therefore require that they can overcome stresses in multiple habitats. Exposure to stress, even at seemingly mild levels, can result in negative effects on subsequent stages of the life-cycle [23]. Consequently, a comprehensive understanding of the sensitivities of all life-stages, from planktonic (fertilization, embryos, larvae) to benthic/pelagic (juveniles, adults) in a changing ocean is vital if we are to identify vulnerabilities that can threaten species persistence in the future.

Reported effects of ocean acidification on fertilization success are highly variable, ranging from none to very negative effects. This variation reflects biological reality – some species are much more tolerant than others – however, it almost certainly also results from different experimental approaches [24,25]; for example, relating to different source populations [25,26], the concentration of gametes [27], the number of parents [28], and the dominance of different parental genotypes in mass spawnings [29]. Such variability has been noted in recent meta-analyses[30-32]; in particular, variability can be enhanced when organisms are exposed to experimental conditions as part of a multi-species assemblage, where species-species interactions and indirect effects also become important [32]. Importantly, fertilizations using gametes pooled from multiple parents, mimicking the multiple spawner scenario in the field, show some resilience to near-future (~pH 7.8) ocean acidification conditions [33-35], as opposed to single crosses [36-40]. High variability in responses of single crosses to ocean acidification also highlights the potential for selection and genetic adaptation, supporting the concept of winners and losers in the face of changing ocean conditions [37-39].

Key Messages: 5.1.2

1. Impacts of ocean acidification upon fertilization success are highly variable, and highlight the potential for genetic adaptation

2. Ocean acidification is generally detrimental for calcifying larvae

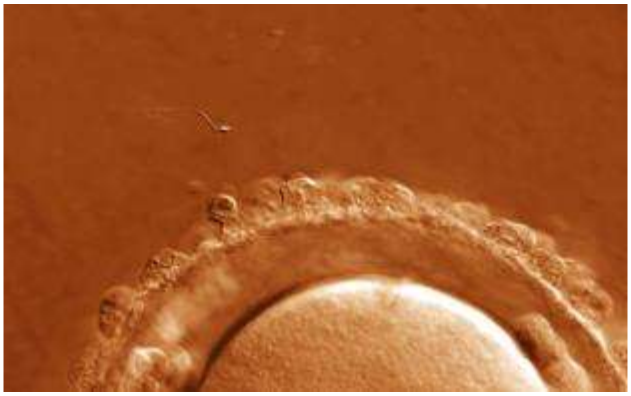


Figure 5.3. Sperm and egg of *Ascidia mentula*. Image courtesy of Jon Havenhand.

The responses of isolated sperm to ocean acidification within the range of near future projections is also variable. Acidification reduces the percentage of motile (i.e. moving) sperm (but not swimming speed) in one species of sea urchin [38], increases sperm swimming speed in a different echinoid species [41], has variable and non-linear effects on both sperm motility and swimming speed in a polychaete worm [26], and no effect on sperm swimming speed in an oyster [37]. Established theory shows that reductions in sperm speed and motility would reduce fertilization success. On the other hand increases in temperature have been seen to have a stimulatory effect on sperm swimming and enhance fertilization success [35,42,43]. Overall, ocean acidification can cause a reduction in fertilization at low sperm concentrations in some species but not others, and responses vary markedly among populations.

Prelarval stages - The few studies that have investigated the effects of ocean acidification on the very earliest embryos (pregastrula) have not detected any negative effects at projected near-future levels [44-46]. Additional work is required to illuminate the possibility that acidification (and warming) are selecting a robust subset of progeny that possess phenotypic/genetic variation appropriate to changing ocean conditions.

Development of larvae and juveniles - Larval shells are among the smallest and most fragile shells in the ocean and are potentially extremely vulnerable to decreased mineral saturation caused by ocean acidification. Consequently most studies have focused on calcifying larvae [32,46-51]. Increased pCO_2 within the range of near future projections is in general negative to calcifying larvae, including mollusc veligers and sea urchin echinoplutei [46,52-55] (Figure 5.4). In studies where several pH levels were tested, deleterious effects (smaller or abnormal larvae, lower weight juveniles) are evident at pH 7.8 (0.3 to 0.4 pH units below ambient). One study reported reduced growth in bivalve larvae with just a slight decrease to pH 8.0 [53]. Oyster larvae may be particularly vulnerable with emerging evidence that pH declines of 0.4 to 0.7 units can induce mortality rates of 80 to >90% [56]. Mollusc larvae with unprotected external skeletons directly exposed to changing ocean chemistry may be more sensitive to increasing ocean CO_2 compared with echinoderm larvae that have internal skeletons protected by overlying tissue. In the latter, hypercapnic (increased organism pCO_2) alteration of metabolism can also have a negative effect on larval growth and calcification [57-59]. Warming (up to the thermal limit) may ameliorate the negative effects of acidification on growth in marine calcifiers by stimulating growth in addition to changing CO_2 solubility [55,60-62], but increased temperatures may also exacerbate detrimental impacts of ocean acidification [63].

In general, non-calcifying larvae, including coral and some sea star larvae, are more resilient to near future acidification [64-68]. However, non-calcifying species (e.g. polychaetes) also show negative responses to acidification [26], and long term experiments show that acidification of the parental environment can lead to impaired larval growth in species that are "robust" in shorter term experiments [65,67]. Interestingly, crustacean larvae with poorly calcified exoskeletons (e.g. amphipods, barnacles, crabs) appear tolerant to acidification [61,69-72].

There is less information on the impact of increased ocean pCO_2 and temperature on the metamorphic transition to a benthic life in marine invertebrates, or on the early juvenile stages. The transition to the benthos may be affected by the negative effect of high CO_2, as shown by reduced coral larvae settlement [73]. Deleterious effects of ocean acidification (through smaller or lower weight juveniles) have also been reported for corals, bivalves, polychaetes and echinoderms [26,74-79], with emerging evidence that current CO_2 values compared to pre-industrial levels could already have caused a reduction in some larval sizes [79]. Reduced larval size in a high pCO_2 ocean would have a negative impact on feeding and swimming ability and make larvae more vulnerable to predation.

By contrast, no effects of near-future acidification were evident for juvenile bivalves *Mercenaria mercenaria*, well-fed juvenile *Mytilus galloprovincialis* [77], or *Mytilus edulis* [80]. Tolerance of these species to acidification may reflect the adaptation to life in low pH and highly variable environments [80]. Juvenile crustaceans are comparatively tolerant of acidification [70,72], although again there is variability [81-83].

Understanding how effects at early life-stages can "carry-over" [23] to influence growth and reproduction of the adult remains a significant challenge and knowledge gap.

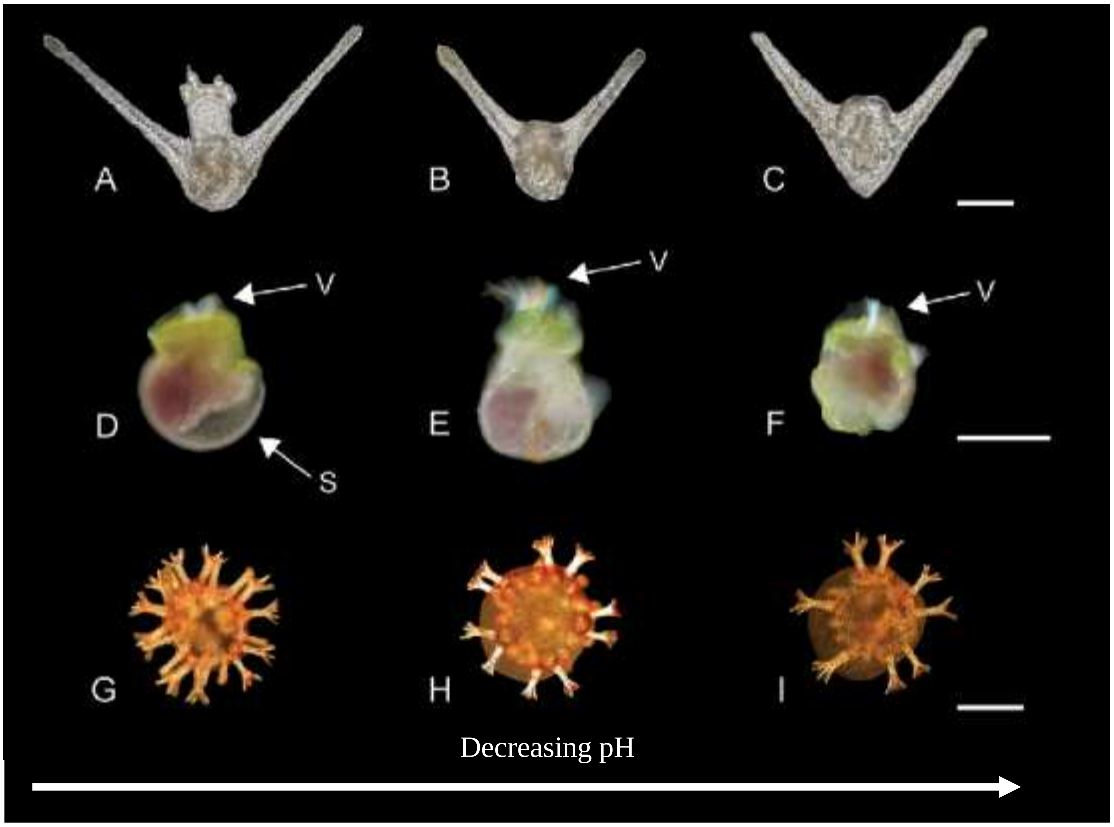


Figure 5.4. A-C. Two-armed echinoplutei of the sea urchin *Centrostephanus rodgersii* reared in controls (A, pH 8.2/21°C) and smaller larvae from experimental (B, pH 7.8/21°C, C, pH 7.6/21°C) conditions. D-F. Veliger larvae of the abalone *Haliotis coccoradiata* reared in control (D, pH 8.2/20°C) conditions with a well-developed shell (arrow) and larvae reared in experimental (E-F, pH 7.8/20°C - pH 7.8/22°C) conditions lacking a shell. G-I Juvenile *Heliocidaris erythrogramma* reared in control (G, pH 8.2/20°C) and experimental (H, I pH 7.6/ 24°C) treatments, the latter showing abnormal calcification as seen in the reduced number of spines. Scales 100 µm. Source: Byrne et al. 2012.

5.1.3. Sensory capacity and behaviour

Ocean acidification can have significant direct and indirect effects on the behaviour of marine organisms. A potentially serious consequence of rising $p\mathrm{CO}_2$ is that it can affect sensory systems and behaviour of marine fishes and some invertebrates [84,85] (Figure 5.5). Reef fish larvae exposed to elevated CO_2 lose their ability to discriminate between ecologically important chemical cues, such as odours from different habitat types, kin and non-kin, the smell of predators [86,87], and visual function [88,89]. Response to auditory cues is altered [90], behavioural lateralization is lost [91] and fish are no longer able to learn [92]. Impaired ability to discriminate between olfactory and auditory cues, or attraction to inappropriate cues, could have serious consequences for ability of larvae to successfully transition from the pelagic to benthic environments. Furthermore, larvae exposed to elevated CO_2 exhibit bolder and more risky behaviour once they settle to the reef, potentially leading to higher mortality from predators [93,94]. Behavioural effects are not restricted to larvae and juveniles. Recent experiments have shown that

Key Messages: 5.1.3

1. Ocean acidification can alter sensory systems and behaviour in fishes and some invertebrates

2. Impacts include the loss of ability to discriminate between important chemical cues adult reef fish also suffer impaired olfactory ability and altered behaviour when exposed to elevated pCO_2, with potential effects on predator-prey interactions [95,96], habitat selection [97] and homing to resting sites [98]. A wide range of reef fish species appear to be affected [94], including important fisheries species such as the coral trout *Plectropomus leopardus* [99]. Impaired behaviour at all life stages occurs as a result of permanent exposure to CO_2 levels ≥ 600-700 µatm CO_2, well within the range that could occur in the ocean this century. The ecosystem effects of impaired sensory behaviour, altered predator-prey interactions, and changes in behavioural attributes is unknown, but has the potential to be significant, including for functionally and economically important species.

Figure 5.5. Altered behaviour of larval damselfish when exposed to elevated CO_2; individuals were more active and ventured further from shelter. Munday et al. 2012[85].

Elevated pCO_2 alters fish behaviour, and possibly invertebrate behaviour, by interfering with brain neurotransmitter function [100]. Sustained exposure to elevated CO_2 induces acid-base regulatory changes in fish that could affect the function of GABA-A receptors, a major inhibitory neurotransmitter. The GABA-A receptor is an ion-channel with conductance for chloride (Cl^-) and bicarbonate (HCO_3^-), and these two ions are also important to acid base regulation in fish. Given the ubiquity of GABA-A receptors in marine organisms, there is good reason to suspect that elevated CO_2 levels could cause behavioural abnormalities in a wide range of marine organisms. One example of GABA-A alteration causing behavioural problems is in the Rockfish *Sebastes diploproa* [101], which became more anxious under future ocean acidification conditions. Interestingly, sensory behavioural 'compensation' may partially reduce detrimental impacts of ocean acidification with regard to anti-predator responses [102]. With regard to GABA-A receptors, other organsims that use Cl^- and/or HCO_3^- to maintain their acid-base balance when exposed to elevated CO_2 may be at particular risk, and some invertebrates that are weak acid-base regulators suffer metabolic depression when exposed to high CO_2 [103,104]. Reduced metabolic rate could also influence a wide range of behaviours in these species.

A critical question in assessing the impact of behavioural changes in marine organisms is whether individuals and populations will be able to acclimate or adapt to rising concentrations of CO_2. There is some hope that adaptation by selection of tolerant genotypes may occur, because larval damselfish reared at 700 µatm CO_2 exhibit considerable variation in responses to olfactory cues, with approximately half of the larvae responding like unaffected controls [93]. These individuals have much higher survivorship when exposed to predators compared with the individuals that are significantly affected by 700 µatm CO_2 [105]. If this variation has a genetic basis, we might expect rapid selection of tolerant individuals throughout the population. Understanding the basis of variation in responses to elevated CO_2 among individuals will be key to making predictions about the potential for adaptation to rising CO_2 levels.

5.1.4. Immune responses and disease

Key Messages: 5.1.4

1. Impacts of ocean acidification upon immune responses and disease is an emerging field, and only few studies have been performed to date

2. Future ocean acidification has the potential to impact immune functions in marine organisms

3. It is unknown whether future environmental change could also affect the virulence and persistence of pathogens

The majority of early research on the effects of ocean acidification on marine organisms has focussed on whole organism, or end point measures of impact – from assessments of increased mortality to changes in growth rate or calcification. More recently however, there has been the realisation that whilst many organisms can acclimate to increases in environmental pCO_2 at relevant timescales, this acclimation might take place at a cost to other physiological processes, such as reproductive investment, immune function, or activity/ecological function.

As a consequence, recent work has considered impacts of ocean acidification on other physiological responses, such as the maintenance of immune function. To date, this work has focussed on commercially important species (crustaceans and molluscs), which are being increasingly seen as important for the maintenance of global food security [106].

Elevated pCO_2 can impact the immune system of marine organisms indirectly, especially if the changes have a negative impact on protein synthesis rates, thus reducing the synthesis of key immune enzymes and peptides. Immune system maintenance has conventionally been regarded as an energetically expensive constraint on an organism's energy budget [107], and it has been speculated that even chronic moderate reductions in pH [108] could be significant, especially in resource limited environments. However, early published work in this area has tended to only consider short-term or acute impacts, which are of limited value in making predictions of the impact of climate relevant increases in sea water pCO_2.

Few studies have gone beyond initial acute shock responses to consider immune impacts once acclimation to the modified environment has taken place, but the limited few have identified that there is a significant impact upon bivalve haemocyte functionality [109], acidosis and phagocyte numbers in echinoderms (variable between species) [110] and that over 6 months, immunity was impaired in sea stars as evidenced by reduced phagocytic capacity [111]. As environmental factors play a significant role in determining the course of infection [7], climate change has the potential to increase susceptibility to disease [112]. From the limited number of examples that are available above it can be concluded that there is the *potential* for future OA to have an impact on the immune function of marine organisms, particularly with reference to commercially important shellfish. It could be speculated that this will result in an increased incidence of disease, particularly when combined with other stresses typically associated with aquaculture.

In conclusion, early research using short-term exposure experiments has suggested that there may well be direct and indirect impacts on the immune function of marine organisms in a future climate. As this field matures, it is imperative that more effort should focus on identifying the long-term (months to years) impacts of climate-relevant increases in pCO_2 to immune function in marine invertebrates, especially in resource or energy-limited environments. Future efforts should also establish the impacts to disease resistance using live pathogen infections, to establish the real endpoint of immune system perturbation (mortality), whilst acknowledging that environmental change can simultaneously affect the virulence and persistence of pathogens [113].

5.2 Benthic communities

Key Messages: 5.2

1. Responses are highly variable, but many benthic species generally have lower growth rates and survival under projected future acidification

2. For corals, many studies show reduction in growth and increased sensitivity with ocean acidification, but this response is variable

3. Most adult molluscs are negatively impacted by ocean acidification, but some species can live in low pH

5. Many macroalgae species are tolerant or may benefit from future ocean acidification

Benthic ecosystems comprise some of the key ocean communities that we rely upon for food and ecosystem services, and occur throughout the world's ocean from the splash zones of all shores to the deepest waters. While none will be immune to ocean acidification, it remains unclear how changes in ocean conditions will affect the composition and function of benthic communities in different environments.

Although environmental conditions are largely constant through time in the deep waters of the sea, there is considerable spatial variability, as carbonate chemistry of deep-sea waters is strongly related to large-scale thermohaline circulation patterns. Consequently, abyssal pH is ca. 0.2 pH units lower in the Pacific than in the Atlantic. Basin scale differences in carbonate saturation are even larger. Whereas the aragonite saturation boundary (the depth at which seawater is corrosive to aragonite) is deeper than 2000 m for much of the North Atlantic, in the N.E. Pacific it shoals to ca. 200 m depth. Deep-sea benthic communities are, by far, the most widespread and abundant benthos in the world's oceans, and are expected to be particularly vulnerable to ocean acidification.

Benthic communities will be affected by the direct and indirect responses of its inhabitants to low pH, reduced carbonate saturation, or related parameters. Meta-analyses of laboratory and field experiments [31,32, 114], and observations in naturally high-CO_2 marine environments [115,116] have shown lower rates of growth, survival, or other performance measures for many benthic organisms in acidified waters, although with considerable variability between species and higher taxonomic groups. Many other factors and indirect effects contribute to sensitivity to ocean acidification [32], including biological processes that may offset potentially detrimental impacts [118].

A recent meta-analyses [31] compared responses of benthic organisms at different CO_2 concentrations: the commonest response up to around 1000 ppm was a negative impact; at higher concentrations the proportion of negative impacts increased greatly (Figure 5.6). Crustaceans appear less sensitive to smaller increases in CO_2 than other groups (Figure 5.6) [32,117], and may be affected through indirect influences, such as effects on food palatability[83]. Their tolerance appears to include juvenile as well as adult growth stages, although there is variability (see early life section). Further discussion below focuses on the more sensitive taxa, corals, echinoderms and molluscs (Figure 5.6).

The sensitivity of entire benthic communities to ocean acidification is also expected to be linked to the scale of natural variation in the environment. Populations inhabiting highly variable habitats, such as coastal systems may possess the phenotypic and genetic diversity to tolerate and perhaps thrive across the range of variation in carbonate parameters. Observations of pH variability from coastal and open ocean sites show large differences in the magnitude of variation [119], with only small variation (< 0.1 pH units) in the open ocean over 30 days, but large daily variation (up to 0.8 pH units) at coastal sites over a single day, driven principally by the photosynthesis / respiration balance. It is therefore crucial that future studies expand upon current research to represent and compare different habitats globally.

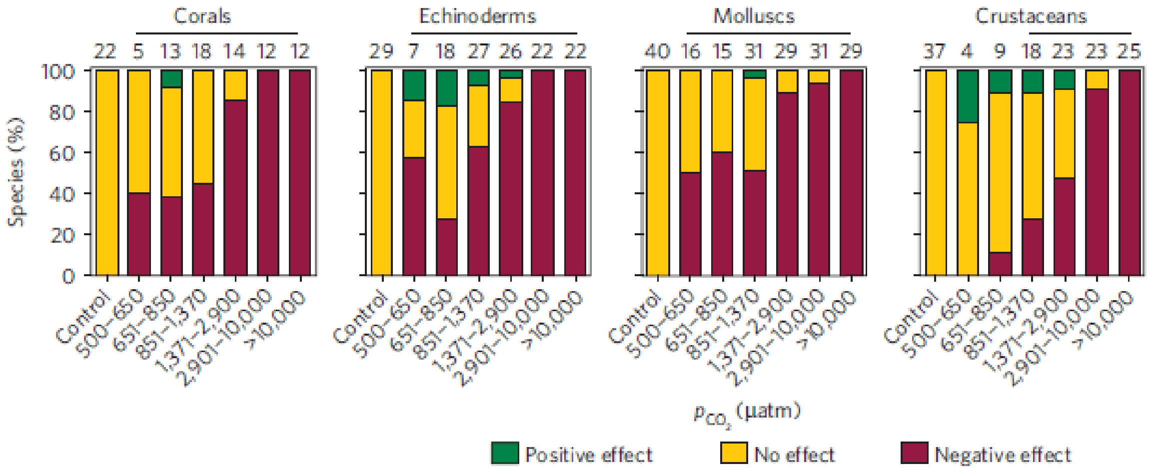


Figure 5.6. Sensitivity of animal taxa to ocean acidification. Fractions (%) of corals, echinoderms, molluscs and crustaceans exhibiting negative, no or positive effects on performance indicators reflect individual fitness in response to increased CO_2. Bars above columns denote count ratios significantly associated with pCO_2. Modified from Wittmann and Pörtner [31].

Understandably, organisms which can create substantial calcifying structures, such as coral reefs, calcifying algae and polychate structures, are considered key habitats to study, as they support substantial associated biodiversity and provide other functions such as coastal protection. Coral reefs are the best studied and one of the best known examples of calcareous structures, and as such have received most research attention to date. However, other structures, such as vermitid reefs (built by gastropods and coralline algae) can have impaired recruitment and increased dissolution under future CO_2 scenarios [120]. Considering the socioeconomic and ecological importance of calcareous structuresother than coral reefs, it is also of high importantance that they undergo further research.

5.2.1. Corals

Tropical coral reef ecosystems represent one of the most biodiverse habitats in the oceans, being home to about a third of all marine species [121,122]. Occurring in both cold and warm-water environments, stony corals are key engineers of the coral reef ecosystem, contributing to the reef's structural framework and the exchange of nutrients between several trophic levels [123]. In light of their ecological and economic importance at regional and global scales, corals are one of the most intensively studied groups of calcifiers in terms of their calcification response to ocean acidification.

Cold-water corals, also often referred to as deep-water corals, are found in all of the world oceans, [124-126], with new information on their distribution being updated through national mapping programmes such as MAREANO in Norway (www.mareano.no), The Deep Sea Coral Research and Technology Program (USA), and through European Community projects including HERMES, HERMIONE and CoralFISH. Figure 5.7 demonstrates the distribution of framework forming cold-water corals such as *Lophelia pertusa*, but does not represent the occurrence of the myriad of other cold-water coral species. Many cold-water coral species require hard substrate for attachment and growth, and in general they thrive where there are strong currents that supply them with food, disperse eggs, sperm and larvae, remove waste products and keep the surfaces of the coral free of sediments. This means that they are often found on parts of the continental slope or on the summits of seamounts where currents are strongest. It has often been assumed that these deep-water habitats are relatively stable in terms of their carbonate chemistry, but recent evidence suggests that within and between habitats, a significant amount of variability can exist, even on a daily basis [127,128].

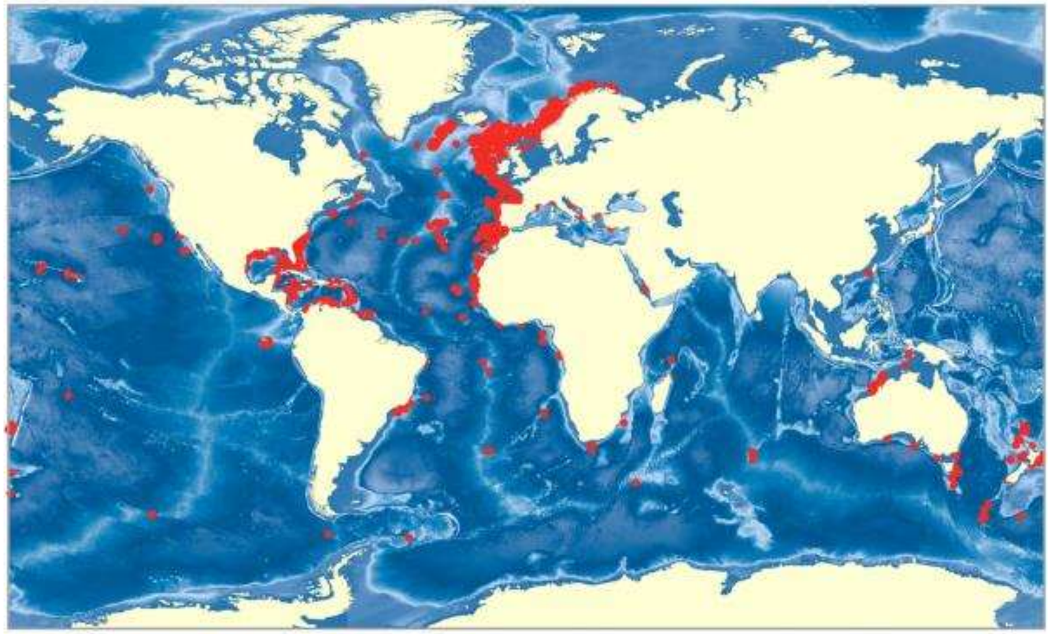


Figure 5.7. Global distribution of reef framework–forming cold-water corals. Source: Reefs of the Deep [129]. Reprinted with permission from AAAS.

Cold-water coral reef systems are often structurally complex environments including gorgonians, stylasterid corals (lace corals), sponges and a variety of fish and invertebrates in the Arctic and sub-Arctic [130,131], and are defined as vulnerable marine ecosystems (VMEs). Impact or damage to these VMEs may lower the local biodiversity and diminish the possibility for many species to find shelter and feeding grounds.

Due to the uptake of anthropogenic CO_2 in the ocean both the aragonite saturation horizon (ASH) and calcite saturation horizon (CSH) (see sections 1 and 3) are becoming shallower. In places, *Lophelia pertusa* already lives very close to the ASH, for example in the Gulf of Mexico [132]. By the end of the century, many deep-sea corals are predicted to be in calcium carbonate undersaturated water [133,134]. Guinotte et al. [133] estimated that > 95 % of corals were above the depth of the ASH in pre-industrial times (year 1765), but by the end of the century, only ~30 % of coral locations will be found above this saturation depth (Figure 5.8). While gorgonians and stylasterids have not been well studied with regard to ocean acidification compared to *Lophelia pertusa*, their calcium carbonate and proteinaceous structures also merit further attention with regard to ocean acidification.

The limited evidence available for how ocean acidification will impact CWCs such as *Lophelia pertusa* indicates that in the short term, projected decreases in pH can decrease metabolism and growth [135-137], but over 6-12 months, *L. pertusa* does not display reductions in growth when subjected to predicted end of the century CO_2 conditions [136,138]. However, these long-term experiments still do not account for any impact on future reproduction of cold-water corals, so the question remains whether key species such as *L. pertusa* can merely temporarily tolerate future conditions, or whether they can thrive under projected future climates. The current low abundance of cold-water corals below the ASH suggests not, and that potential increased energetic demands for living below the ASH cannot usually be met.

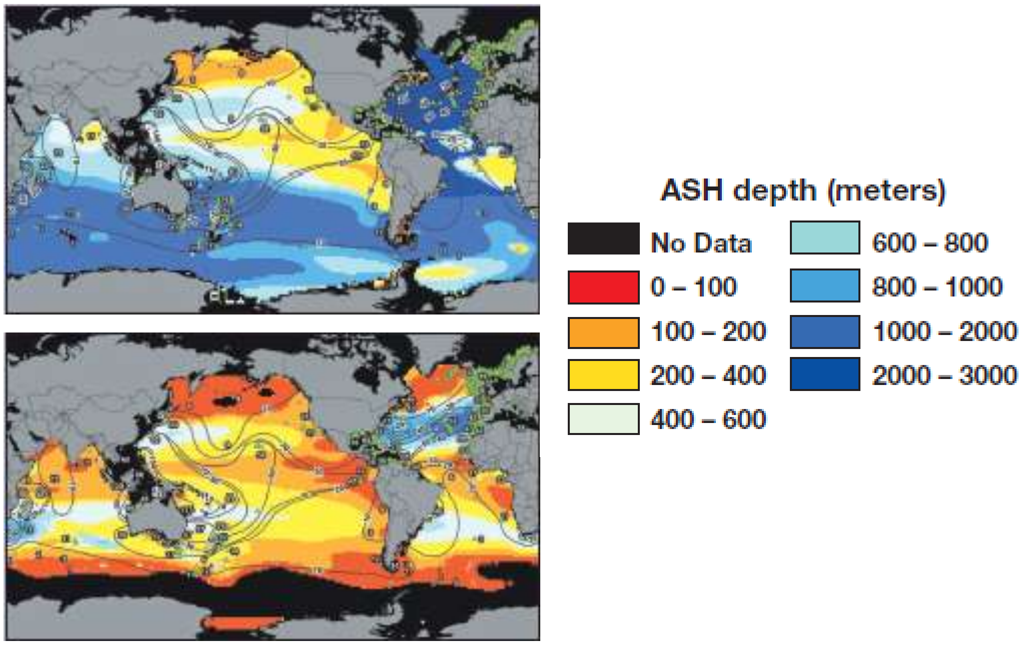


Figure 5.8. Depth of aragonite saturation horizon (ASH) and locations of deep-sea corals (green triangles). Top: Projected ASH depth for year 1995; pCO_2 = 365 ppmv. Bottom: Projected ASH for the year 2099; pCO_2 = 788 ppmv. Black areas appearing in Southern Ocean and North Pacific in bottom panel indicate where ASH depth has reached the surface. Contours indicate diversity for 706 species of azooxanthellate (without microalgal symbiont) corals. Numerals not falling on diversity contours indicate number of azooxanthellate coral species. Guinotte et al. [133].

The ability and long-term sustainability of cold-water corals to survive and thrive below calcium carbonate saturation depths such as those noted by Thresher et al. [139] thus remain debated. Although scleractinian corals can up-regulate their extracellular pH within the calicoblastic layer at the sites of calcification through energy intensive processes [18,140-142], the regulation only applies for coral skeleton that is covered by living coral tissue. CWC framework reefs are typically composed of a significant amount of bare, dead skeleton beneath the living material (Figure 5.9), which would start to dissolve in undersaturated conditions, and be eroded with increased efficiency by bio-eroding sponges [143]. Thus future changing conditions could potentially have large impacts upon current CWC habitats and associated biodiversity.

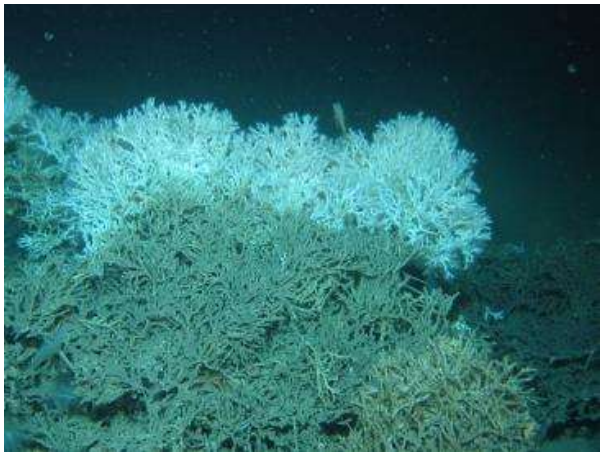


Figure 5.9. Image of live *Lophelia pertusa* with underlying dead framework (Rockall Bank, NE Atlantic). Source: Changing Oceans 2012.

For tropical corals, many studies demonstrate a reduction in growth (net calcification rates) in response to ocean acidification [144-148]. However, this is not a ubiquitous response, with different species exhibiting negative [149], no measureable response [150], or variable responses [144] to reduced pH [151]. Examining coral growth rates through time by analysing coral cores remains difficult, due to ontogenetic effects and growth variability from coral age and size [152]. Furthermore, responses may be non-linear, such that there may be no response until a 'tipping point' is reached [153].

Meta-analysis has proved very useful in synthesizing the data obtained from these multiple studies, and in identifying the factors that may explain variation between them [30,32,154,155]. The general conclusion of these analyses and other reviews [13,156-158], is that corals are sensitive to ocean acidification, with declines in coral calcification associated with declining aragonite saturation state and seawater pH (see Figure 5.10). However major questions remain notably *how* and *why* coral calcification is sensitive to ocean acidification. This is the subject of recent research initiatives that investigate the mechanism of calcification.

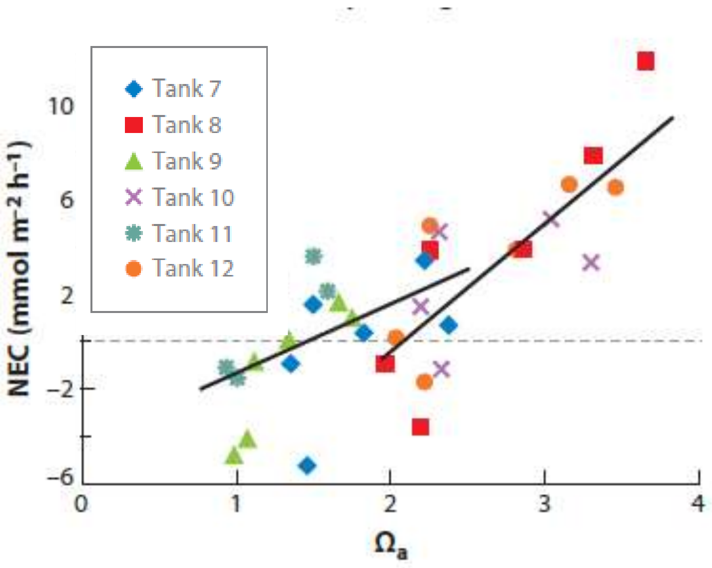


Figure 5.10. Net ecosystem calcification as a function of aragonite saturation state of experimental sub-tropical coral mesocosms dominated by the coral *Montipora capitata* over a 24h period. Tanks 8, 10 and 12 were exposed to ambient conditions, and tanks 7, 9 and 11 were exposed to double ambient pCO$_2$. Growth rates decline with decreasing aragonite saturation, even though saturation states are >1. Source: Andersson et al. [158] with data from [159].

Insight into the physiological mechanisms that corals use to cope with ocean acidification may explain inter-species differences in sensitivity, and may help to predict winners and losers in a higher CO$_2$ ocean. For example variation in the capacity to regulate ions/ pH under ocean acidification may be a defining physiological trait that facilitates future survival, and there is emerging evidence in coral skeletons that suggests that the extent to which corals can upregulate pH varies from species to species [160]. Additionally, research has already indicated that temperature and ocean acidification can act synergistically for some species to reduce calcification rates more than ocean acidification acting alone [15], so future studies have to consider multiple stressors to determine the future fate of these key ecosystems.

5.2.2. Molluscs

Bivalve molluscs were identified in early ocean acidification research to be particularly challenged by ocean acidification (see Gazeau et al. [161] for a review), and indeed a large fraction is negatively impacted by even relatively low levels of ocean acidification (Figure 5.6); similar to echinoderms [31]. This can lead to knock on effects such as increased predation for smaller oysters [162]. However, for some species, while acute experiments without an acclimation period result in strong reductions in calcification [163], longer-term incubations with realistic food regimes demonstrated that significant calcification can be maintained even when the seawater is undersaturated with respect to calcium carbonate, such as for adult mytilid mussels [164-166]. In fact, mussels (*Bathymodiolus brevior*) have been found close to deep-sea hydrothermal vents, growing at pH values between 5.4-7.3. While this feature indicates great biological control over the calcification process, Tunnicliffe et al.[167] also suggest a fundamental role of the external organic cover, the periostracum, in enabling persistence at such stressful locations. A similar role of the periostracum has been suggested for coastal *Mytilus edulis*, which can also calcify at very high rates when calcium carbonate is undersaturated [165]. Results from a coastal enriched CO_2 habitat, the Western Baltic Sea, indicate that successful settlement and dominance of mytilid mussels and other calcifying invertebrates is possible at seawater $p\mathrm{CO}_2$ values similar to those projected for the end of the century [80,165]. Where reductions in growth and calcification are observed, energy budget reallocation may be the cause [168], or potentially increased oxidative stress [169]. Future research should thus focus on determining cellular energy budgets to analyze energetic trade-offs.

The impact of ocean acidification to larval stages of bivalves is also of great importance to their continued survival, especially since larval bivalves and heavily calcified pelagic larvae of other molluscs have been shown to be sensitive to ocean acidification [77,170,171]. This topic is covered in more depth in section 5.1.2.

5.2.3 Echinoderms

Echinoderms have been extensively studied with respect to sensitivity to simulated ocean acidification, and in particular with respect to their larval stages (see section 5.1.2 for more details on echinoderm larval stages). Briefly, while early life stages of some species have been shown to react with severely increased mortality to ocean acidification [52], most species respond with slight reductions in larval growth [48,59].

When exposed to simulated ocean acidification, echinoderms experience energy budget reallocation, with only few examples of increased mortality [172]. While moderately elevated pCO_2 (<1,000 µatm) has led to increased feeding and growth rates in intertidal sea stars [173], other studies identified reduced investment in growth, calcification, reproduction or immunity [111,174-177]. Despite studies highlighting the key modulating role of long-term, trans-generational and adaptive responses of echinoderms to ocean acidification [48,178,179][59], little research attention has been devoted to these factors and future studies should reflect this.

5.2.4 Seagrass and macroalgae

While seagrass and macroalgae generally grow in coastal waters and experience diel pH changes, their responses to ocean acidification depend upon their distribution and species. Macroalgae can be calcareous or non-calcareous and form an important component of many coastal ecosystems [180], and many macroalgae species are known to be tolerant to or benefit from future ocean acidification [116,180-185] (Figure 5.11). While ocean acidification can be detrimental to the calcifying species, the enhanced CO_2 can also increase productivity in calcareous and non-calcareous species alike (see Johnson et al. [183]). It is also important to note that seagrass dominated areas can also substantially modify their own seawater carbonate chemistry environment through primary productivity [186], and that the complex interaction between multiple stressors such as eutrophication and hypoxia in coastal waters in general may lead to faster declines in pH with increasing atmospheric CO_2 [187].This leads to substantial diel variability in seawater pH [188,189]. In the case of tropical seagrasses, they could potentially benefit adjacent coral reef systems by elevating pH by up to 0.38 at tidal intervals [188].

Although ocean acidification is generally detrimental to calcareous algae [190,191], some species like *Padina* spp. have been found to thrive under naturally high CO_2 conditions even after decalcification [183], although this may be due in part to a concurrent decrease in grazers. The role of grazers and species interactions may thus be an important aspect for future studies to consider in more depth, as there is also emerging evidence that high CO_2 can decrease the production of protective phenolic substances used to deter grazers [192].

Figure 5.11. Seagrass and a natural CO_2 seep. Source: Giorgio Caramanna.

Key Messages: 5.3

1. Non-calcifying phytoplankton may benefit from future ocean acidification

2. Calcifying phytoplankton such as coccolithophores exhibit variable responses to future ocean acidification

3. Mesocosms combining both calcifying and non-calcifying phytoplankton demonstrate enhanced net carbon uptake by phytoplankton under elevated CO_2

4. Bacterial responses to ocean acidification are uncertain, but any changes will have implications for nutrient cycling

5. Planktonic foraminifera and pteropods are likely to experience decreased calcification or dissolution under projected future conditions

6. Decreases in planktonic foraminifera shell thicknesses and sizes may decrease efficiency of future carbon transport between the sea surface and seafloor

5.3 Pelagic communities

5.3.1. Plankton

Plankton play an important role in marine ecosystems, and is comprised of phytoplankton (photosynthetic plankton), zooplankton (which includes organisms that spend their whole life in the water column as well as juveniles and gametes of many benthic organisms), and bacteria. These plankton (calcifiers and non-calcifiers) form a key component of the marine food chain and also play an important role in biogeochemical cycling.

Biocalcification (by both phyto- and zooplankton) affects the ocean carbon cycle by assisting the export of organic matter out of the upper ocean and its burial in deep-sea sediments. Sedimentologists studying the flux of particles collected in deep-sea sediment traps have found that “ballasting” of organic matter aggregates by biominerals may facilitate the flux of organic carbon from the upper ocean to the seafloor [193,194]. If there is a significant decrease of biocalcification by planktonic organisms as a result of ocean acidification, then a likely secondary effect is reduced export of organic carbon from the surface ocean, and reduction of the capacity of the ocean to buffer the rise in anthropogenic carbon dioxide (also see section 5.4.3).

Phytoplankton and bacteria

Non-calcifying phytoplankton - These organisms form a significant proportion of the phytoplankton and includes diatoms, cyanobacteria and dinoflagellates. Many Harmful Algal Bloom species (HAB). Stimulating effects of increased CO_2 on photosynthesis and carbon fixation have been noted in all of these groups [195-198]. Increased CO_2 could also lead to enhanced mitochondrial and photorespiration (which in turn produce CO_2), and therefore the net effect on primary production needs to account for both CO_2 fixation and loss [199,200]. It is hypothesised that an increase in CO_2 will be of overall benefit to phytoplankton, as the increased CO_2 in external seawater will reduce CO_2 diffusion leakage from biological cells (where the CO_2 is concentrated) to the surrounding seawater [195]. However, photosynthetic mechanisms vary widely between photosynthetic organisms [201], and this may lead to a shift in community composition in the future [202,203]. Assessing whether HAB species will be among those which will benefit from future environmental change remains a key focus for future research, as some research suggests that the release of toxic compounds could increase [204,205], or that the lack of carbon concentrating mechanisms in many HAB species will be of benefit to them in future climates (for a full discussion see [206]).

Calcifying phytoplankton - Of the calcifying algae, coccolithophores are perhaps the group, which have received most interest, as they form a major component of the phytoplankton in more oligotrophic waters. They are biogeochemically important as carbonate producers, and are extensively studied by geologists. Chalk is predominantly formed of fossil coccoliths. Coccolithophores are a group of unicellular phytoplankton, which produce calcite plates called coccoliths (Figure 5.16), and cells are typically 5 to 20 µm across but are present in abundances of tens of thousands to millions per liter in most seawater from the photic zone.

Some species of coccolithophores (such as *Emiliania huxleyi*) can readily be grown in laboratory cultures and at least 40 significant research papers on the impact of ocean acidification on coccolithophores have been published. Early experimental work with laboratory cultures and large-scale semi-enclosed field cultures (mesocosms), suggested that there was a clear reduction in calcification with increasing pCO_2 [207-210], with potential synergistic impacts of increased solar UV radiation due to thinner coccoliths [211]. Early experiments did however note that other effects such as growth rate and cell size changes could obscure the response of decreased calcification. This may be due to shifting balances in potential positives and negatives for photosynthesis and calcification. Building on these initial indications of a distinct influence of carbonate chemistry on coccolithophores, several ecological studies suggested that variations in carbonate saturation state might influence aspects of the distribution of modern coccolithophores, such as the timing of blooms [212], and absence of coccolithophores from the Baltic Sea [213] and from parts of the Antarctic [214]. Most strikingly it has been suggested that coccolith mass in *E. huxleyi* and closely related species is controlled by saturation state in both the modern ocean and historically [215].

However, culture work on species other than *E. huxleyi* can show very different responses, with some species showing negligible response to elevated pCO_2 [216]. Moreover it has been shown that even within *E. huxleyi*, the response of different laboratory strains is highly variable, with responses varying from no calcification to increased calcification in response to strongly elevated pCO_2 conditions [217]. Importantly, some studies suggest that coccolithophores may be able to adapt to changing conditions even on the relatively rapid timescales at which they are occurring [218,219]

Conflicting results have also been found from field and geological evidence. Two studies of sediments from the past 200 years have provided evidence for *increased* calcification of coccolithophores over this time period despite the rise in atmospheric CO_2, or even as a counter-intuitive response to it [217,220].

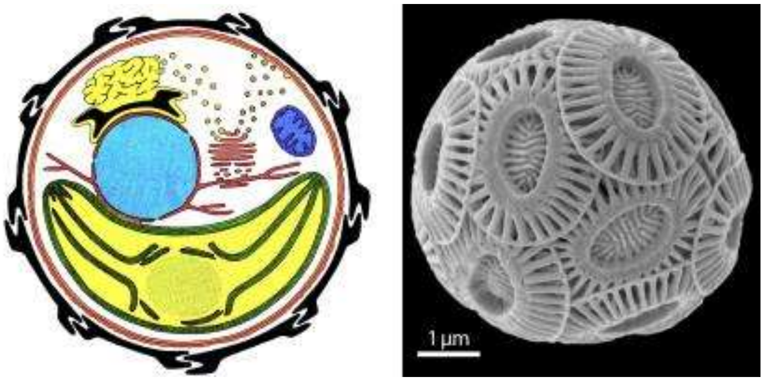


Figure 5.12. Left: Drawing of a single cell of *Emiliania huxleyi* showing coccoliths (black) forming within an intracellular vesicle before being extruded to form the extracellular coccosphere (image courtesy of Peter Westbroek). Right: Scanning electron micrograph of an *E. huxleyi* coccosphere.

Bacteria - While some bacteria are counted among the phytoplankton (*Synechococcus* and *Prochlorococcus*), many do not photosynthesise but can play a key role in nutrient cycling, being 'free-living' or associated with some of the other plankton such as foraminifera. A significant proportion of the phytoplankton-derived organic carbon ends up as dissolved organic carbon (DOC), and this can be taken up by heterotrophic bacteria. The amount and growth of such bacteria determines the fraction of DOC that can be 're-introduced' into the food web through subsequent grazing [195].

Box 5.1: Svalbard mesocosms case study

Large-scale mesocosms provide invaluable data on how communities of both calcifying and non-calcifying organisms will fare under future conditions. Mesocosms have been successfully deployed and used in Svalbard, Norway, to assess impacts of ocean acidification over ecologically relevant timescales under close-to-natural conditions. Results indicated that under high CO_2/ low pH, phytoplankton community composition changed but the microzooplankton community exhibited high tolerance [221]. Importantly, net carbon uptake by phytoplankton was enhanced, but the systems were pushed towards overall negative effects on export potential [222].

Photograph of experimental mesocosms. Source: Maike Nicolai, GEOMAR.

The response of bacteria to projected future changes is relatively unstudied compared to the calcifying plankton, but recent studies on bacteria, which associate as biofilms suggests that future changes will alter bacterial community composition [223]. Future nutrient cycling may also change depending upon whether bacterial communities change significantly as pH decreases, which could have direct impacts upon nutrient cycling between benthic and pelagic ecosystems [224].

Zooplankton

There are two main groups of biocalcifying zooplankton; pteropods and foraminifera, both of which have been the subject of research on the potential effects of ocean acidification.

Pteropods are a group of gastropods (i.e. snails) in the upper layers of the ocean. The normal gastropod foot is modified into a pair of swimming wing-like fins, giving them the common name sea-butterflies, and the shell is also often elaborately modified [225] (Figure 5.13). Pteropods occur throughout the global ocean but they are most abundant in sub-Arctic and sub-Antarctic to Antarctic waters where they can form a significant part of the zooplankton and are important food stocks for fish and other predators [226]. Pteropods have shells formed of aragonite rather than calcite. The combination of thin aragonitic shells [227] and abundant occurrence in the Arctic and Southern Oceans makes them likely to be one of the first groups of organisms to be severely affected by ocean acidification since undersaturation will first occur at high latitudes, a combination of the direct effect of low temperatures on solubility as well as concomitant decreases in carbonate ion concentrations [228].

Early shipboard incubations demonstrated that pteropod shell dissolution could indeed easily occur, which has now been replicated in the Antarctic at $\Omega_{\text{aragonite}} < 1$ [11,228,229]. In addition to no calcification occurring when seawater is undersaturated ($\Omega_{\text{aragonite}} < 1$), it has now also been demonstrated that calcification is inhibited at significantly higher levels of $\Omega_{\text{aragonite}}$ [230-232]. The vulnerability of pteropods to ocean acidification and warming has been demonstrated for the Arctic pteropod *Limacina halicina*, in which shell growth was reduced and degradation increased at moderately elevated temperature and $p\text{CO}_2$ (1100 μatm) [233] despite some regulatory capacity to ameliorate these effects [234], and in the subarctic, where biomass of the dominant pteropod has decreased notably [235]. This has been further confirmed by a modeling study combining predicted aragonite saturation states for the end of the century, with data on the likely impact on pteropod calcification, which concluded that "there appears little future for high-latitude shelled pteropods" [236], which will impact organisms which utilize these as a food source [237].

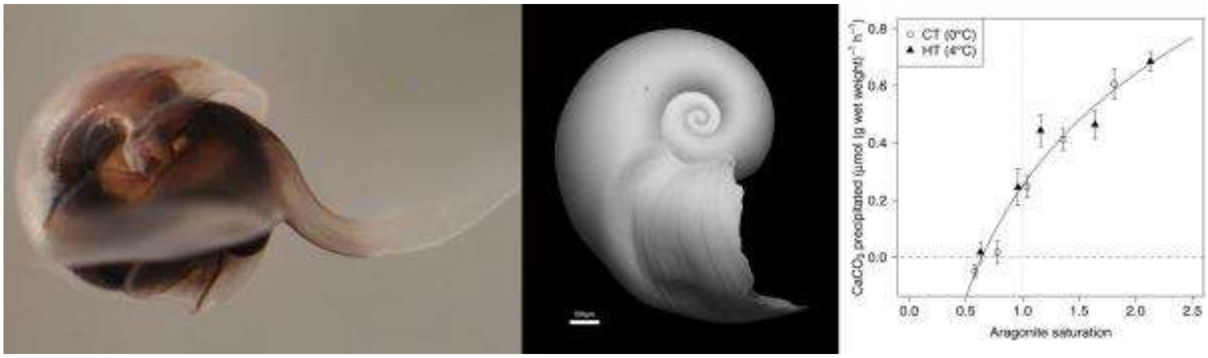


Figure 5.13. Left: A living pteropod from the Arctic (image Vicky Peck, BAS). Centre: The shell of a juvenile pteropod from the South Atlantic. Right: Data from laboratory culture experiments on shell growth rate of *Limacina helicina* incubated under aragonite saturation states equivalent to those seen in the Arctic at present day (ca 2.0) to the year 2100 (<1.0), from Comeau et al. [232].

Foraminifera are a group of unicellular zooplankton forming chambered calcite shells. The shells are elegant structures typically about 0.1 to 0.5 mm across and many species have a halo of delicate radial spines supporting a mass of protoplasm, gas bubbles, and symbiotic algae. Although they usually only form a minor component of the total zooplankton, they leave a prolific record of their existence since their shells sink readily after death and form one of the main components of deep-sea sediments [238]. This makes them important contributors to the ballasting effect, and makes them a group of major interest to geologists, both as rock-forming organisms and as recorders of ocean chemistry.

Laboratory experiments have shown that carbonate concentration has significant impact upon planktonic foraminiferal calcification, with decreases in shell thickness and weight occurring at levels well above $\Omega_{\text{(calcite)}} = 1$ [239-243]. This is also confirmed through geological studies [244,245]. Perhaps most remarkably, field studies comparing modern plankton from the water column with pre-industrial populations in the surface sediment have indicated that marked reductions in shell weight have already occurred [245,246]. Research on tropical benthic foraminifera has also revealed vulnerability to ocean acidification particularly amongst non-symbiont bearing species with hyaline or porcelaneous shells [247].

However, shell mass and thickness is also controlled by other factors such as temperature, depth and gametogenic calcite formation, and to date only a few studies exist on foraminiferal shell mass and thickness. Despite this, and that recent work on pre-Quaternary fossil records of planktonic foraminifera failed to find predicted effects of carbonate chemistry [248], the overall evidence strongly suggests that ocean acidification will have a significant effect on planktonic foraminifera and hence on their role in ballasting organic carbon fluxes.

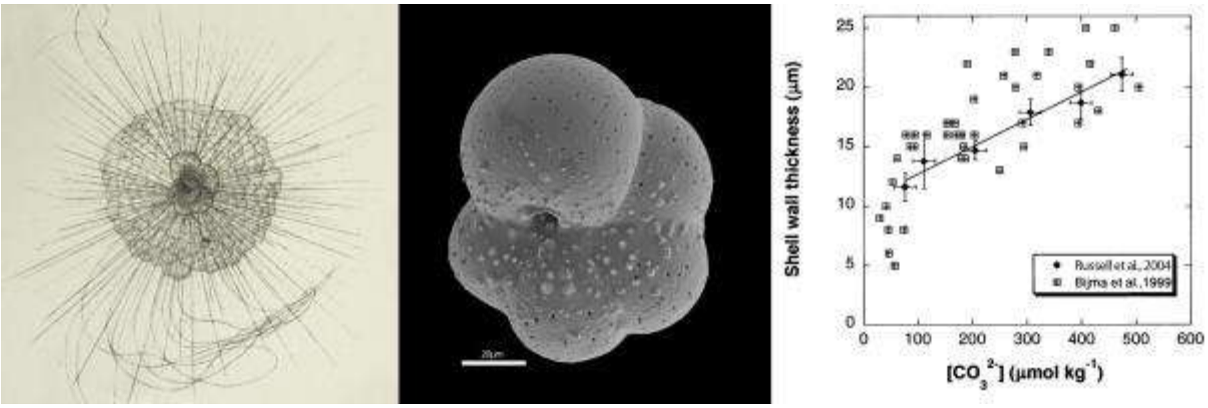


Figure 5.14. Left: Drawing of a modern planktonic foraminifera surrounded by a halo of bubbles and symbiotic algae supported by spines [249]. Centre: Scanning electron micrograph of the shell of juvenile planktonic foraminifera. Right: Laboratory culture data variation in shell wall thickness in *Orbulina universa* cultured under bicarbonate conditions equivalent to those from the modern ocean (ca. 250µmol kg^{-1}) to those anticipated in 2100 (ca. 100 µmolkg^{-1}), and under rather more extreme conditions (from Russell et al. [241]).

Copepods. Direct effects of elevated $p\text{CO}_2$ on copepods have only recently gained attention, and our knowledge on their response to ocean acidification remains limited. Copepods are holoplanktonic crustaceans that have a maximum size of ~1 cm and are the most abundant group in marine zooplankton communities worldwide forming the predominant link in pelagic food webs between primary production and higher trophic levels [250,251] In controlled experiments, reproductive success (i.e. egg production and hatching) decreased at high CO_2 concentrations (>1000 µatm) compared to low CO_2 levels [47,252-256]. However, in Arctic mescosm experiments over thirty days, abundance and stage composition of *Calanus* spp., *Oithona similis*, *Acartia longiremis* and *Microsetella norvegica* did not change with CO_2 concentrations, indicating that possible effects of predicted changes in CO_2 were not strong enough to be reflected in the population dynamics [257], although the grazing rates of *Calanus* spp. decreased with increasing CO_2 [258]. Other, more sensitive species such as *Centropages tenuiremis* increased respiration and grazing rates at 1000 µatm, likley to meet increased energetic demands [259]. Direct effects of CO_2 on copepods and other non-calcifiying heterotrophic plankton may not be as potentially severe as for calcifying organisms. However, if algal biochemical or species composition and thus food quality changes due to increasing $p\text{CO}_2$, limitations in food quality may reduce the reproductive success of copepods [260]. Thus, non-calcifying organisms may also be impacted by ocean acidification via trophic interactions.

5.3.2. Fish, squid and cuttlefish

Nektonic (swimming) organisms are those that can move independently of water currents, as opposed to plankton, which are more passive. Although fish represent the majority of nektonic organisms that have been studied with regard to ocean acidification, cephalopods are also important in terms of abundance and economic value.

Fish are generally considered to be more resilient to direct effects of ocean acidification than many other marine organisms because they do not have an extensive skeleton of calcium carbonate, and they possess well-developed mechanisms for acid-base regulation [104]. Indirect effects of ocean acidification, such as through 'bottom up' changes in the food web, thus need to be considered in future studies as well. Fish compensate for acidosis (increased acidity in blood or tissues) by transport of acid-base relevant ions, mostly across the gills [261,262]. In most species studied to date, almost complete compensation of acidosis occurs within a few hours or days of exposure to elevated CO_2 [2,3,164,262]. This tight regulation of acid-base balance maintains the pH required for efficient cellular function in a high CO_2 environment, but may necessitate additional energy expenditure [263].

Key Messages: 5.3.2

1. Most fish are likely able to maintain sufficient O_2 delivery under future conditions, but cephalopod metabolism may be reduced

2. Ocean acidification causes sensory and behavioural impairment in many fish species

3. Juvenile life stages appear more susceptible to future ocean acidification

One concern is that additional energy expenditure associated with acid-base regulation, or a decline in oxygen carrying capacity associated with incomplete acid-base regulation, may reduce the scope for aerobic performance in fish [264]. While aerobic scope in two tropical cardinalfishes declined significantly at projected future CO_2 levels [265], Atlantic cod maintained their standard and active metabolic rates, critical swimming speeds and aerobic scope after prolonged exposure (4 and 12 months) to even higher CO_2 levels [266]. Furthermore, studies on freshwater and estuarine fishes exposed to CO_2 levels many times greater than end-of-century predictions for ocean pCO_2 have generally found no effect on oxygen uptake or swimming performance [262,263,267]. These results indicate that while sensitivity to elevated CO_2 varies among species, most fish are probably able to maintain sufficient oxygen delivery at CO_2 levels predicted to occur in the near-future.

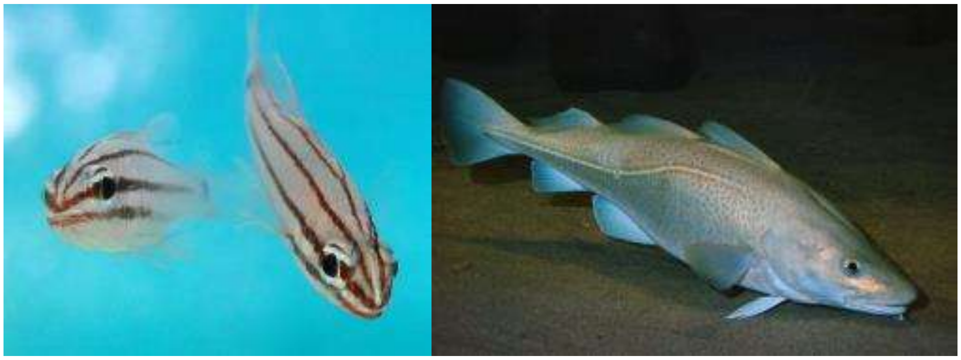


Figure 5.15. Left – The cardinalfish *Ostorhinchus doederleini*. Right – Atlantic cod *Gadus morhua*. Image source Goran Nilsson and animalspot.net

CO_2 effects on cellular energy budgets have scarcely been studied to date, yet it has been shown for Antarctic fish (*Notothenia rossii*) that several weeks of exposure to elevated pCO_2 (2000 µatm) can lead to reduced mitochondrial capacities and putative shifts in metabolic pathways involved in mitochondrial energy metabolism [3]. Increased intracellular levels of bicarbonate, due to both increased pCO_2 and active pH buffering by bicarbonate uptake [262] can lead to competitive inhibition of enzymes of the Krebs cycle (citrate synthase, succinate dehydrogenase) and may elicit transcriptional changes and functional modifications of mitochondrial proteins by activation of a soluble adenylyl cyclase and subsequent action of protein kinase A (PKA) [268].

The effects of ocean acidification on development, growth and survival of marine fishes has largely focused on larval and juvenile stages, because they are predicted to be more sensitive to elevated pCO_2 than adults [104,263]. Despite this prediction, recent studies have found that the early life-history stages of some fishes are resilient to projected future levels of ocean acidification. Development, growth and survival of larvae and juveniles of several reef fish species [269,270], the pelagic cobia [271] and walleye pollock [272] appear relatively robust to near-future CO_2 levels (≤1000 µatm CO_2). In contrast, larval growth declined and mortality increased in the estuarine species *Menidia beryllina* at similar CO_2 levels [273] (Figure 5.16), and tissue development was disrupted in the cod *Gadus morhua* reared at higher CO_2 levels (1,800 and 4,200 µatm CO_2) [274]. However, the eggs and larval stages remained relatively robust under ocean acidification conditions [275], so more work is needed to determine the *Gadus morhua* vulnerability. These studies suggest that the sensitivity of larval and juvenile fishes to rising CO_2 levels is highly variable and that some species will be negatively impacted. However, reduced growth and survival of juvenile anemone fish *Amphiprion melanopus* reared at high CO_2 levels was reversed when the parents experienced the same CO_2 conditions as the juveniles [276]. Therefore, it is premature to conclude that near-future CO_2 levels will have significant negative effects on the growth, development or survival of marine fishes until studies include exposure to high CO_2 during both the parental and offspring generations.

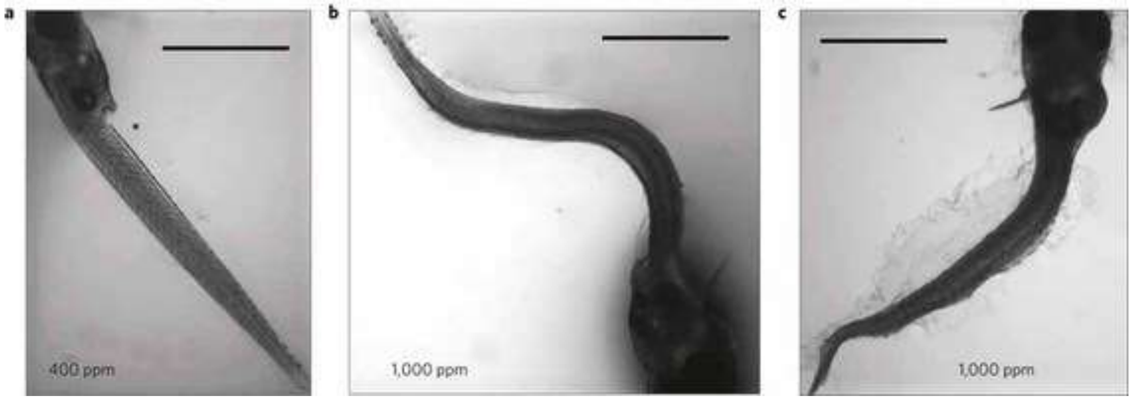


Figure 5.16 Larvae with curved or curled bodies were significantly more common at increased (**b**,**c**) when compared with control (**a**) CO_2 levels. Scale bar=1 mm. Adapted by permission from Macmillan Publishers Ltd: Nature Climate Change (Baumann et al.[273]), copyright (2012).

The effects of chronic exposure to high CO_2 on fish reproduction has been little studied, but preliminary studies have not detected substantial impacts, although long-term consequences in many species remain to be determined [277]. In the short term, reproductive output can be stimulated by high CO_2 in examples such as the cinnamon anemonefish *Amphiprion melanopus* [277], but sperm motility is arrested by mild increases in pCO_2 in some flatfishes [278], but not in the cod, *Gadus morhua* [279], or 11 other species from a range of families [278]. Furthermore, rearing eggs of Atlantic herring (*Clupea harengus*) in acidified water had no detectable effect on fertilization success, embryonic development, hatch rate, length and weight at hatching and yolk size [280]. Sensitivity of fish eggs to elevated CO_2 varies markedly between species, but species tested to date typically have 24h LC50 (lethal concentration resulting in 50% mortality over 24 hours) values well above 10,000 µatm CO_2 [263], which is far in excess of projected end of the century CO_2 levels.

There are three areas in which consistent effects of elevated CO_2 have been detected for marine fish. First, exposure to elevated CO_2 causes sensory and behavioural impairment in a range of marine fish [85]. Second, otolith (earbone) size is consistently larger in larval and juvenile fishes reared under elevated CO_2. Larger ear bones have been observed in larval seabass [281] (Figure 5.17, clownfish [[282], cobia [271] and Atlantic cod [283] reared between 800-1800 µatm CO_2. While the ecological significance of larger otolith size is uncertain, auditory models suggest that larger otoliths could potentially enhance auditory acuity [284]. Thirdly, vision and retinal function appears to be negatively impacted by ocean acidification [88,89,101].

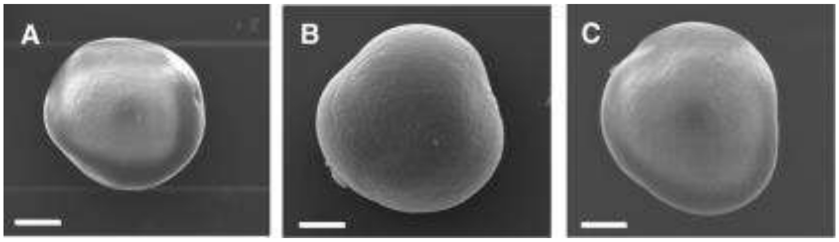


Figure 5.17 Dorsal view of sagittal otoliths of 7-day-old white sea bass grown at (**A**) 430, (**B**) 1000, and (**C**) 2500 µatm pCO_2 in seawater. Scale bars indicate 10 µm. Source: [281]. Reprinted with permission from AAAS.

While results indicate that most fish are probably able to maintain sufficient oxygen delivery at CO_2 levels predicted to occur in the near-future, the effect on squid may be more pronounced. The epipelagic squid (e.g. *Ommastrephidae, Gonatidae, Loliginidae*) are considered to be most severely impacted by the interference of CO_2 with oxygen binding at the gills, as they have a very finely tuned blood oxygen transport system to maintain high metabolic rates using the respiratory pigment haemocyanin [285]. Haemocyanin is very sensitive to CO_2 and as such, blood oxygen transport can be easily disturbed to reduce activity [286,287] as demonstrated in the Pacific jumbo squid *Dosidicus giga,* which had significant reduction of metabolic rates and activity levels under 1000 µatm of CO_2 [288]. Importantly, elevated CO_2 could also affect squid paralarvae, as demonstrated by abnormal shapes of aragonite statoliths in the Atlantic Longfin squid *Doryteuthis pealeii*, which are critical for balance and detecting movement [289].

More research is needed to characterise the effects of ocean acidification and warming on the cuttlefish *Sepia officinalis*, one of the most common and commercially-available cephalopods in Europe. While this species does not appear detrimentally impacted by ocean acidification during some development studies, and even show increased calcium uptake into its cuttlebone [290], *S. officinalis* does display shorter embryonic periods, lower survival rates and enhanced premature hatching when reduced pH is combined with increased temperature [291].

5.4 Impacts on ecosystem services, livelihoods, and biogeochemical cycles

5.4.1 Impacts on ecosystem services

The previous sections show how pH affects different organisms and ultimately biodiversity, but what do these changes mean for society? The implications for society will become apparent if ocean acidification causes changes in the health, abundance or distribution of economically and socially important marine species and the ecosystems that support them [29]. To date, however, scaling-up the effects of pH change from individual organisms to populations, communities and ecosystems has received less attention [103] although this is changing [115,293].

Key Messages: 5.4

1. Ocean acidification has already impacted the provisioning services of some oyster hatcheries

2. Ocean acidification could impact ecosystem services at provisional, regulating, cultural, and supporting service levels

3. Impacts of ocean acidification are estimated to be over USD$1000 billion annually for molluscs and coral reefs by 2100

To examine the societal implications of ocean acidification in more depth, an ecosystem services framework can be used. Ecosystem services are the components of nature that are used (actively or passively) to create human well-being and economic wealth [294]. They result from ecological processes, functions and biodiversity [295], and society is dependent upon them as a life support system as well as for enhancing its well-being [296]. At a general level, ecosystem services can be categorised into four distinct groups [297]: **provisioning services** (e.g. food and fibres); **regulating services** (e.g. gas and climate regulation and bioremediation of waste); **cultural services** (e.g. education, recreation and inspiration); and **supporting services** (e.g. nutrient cycling, primary production and ecosystem resilience) (Figure 5.18).

Supporting services - These comprise the processes and functions that contribute to all other ecosystem services. Any changes in these will have consequences through provisioning, regulating and cultural services. For example, many species that are likely to be negatively impacted by pH changes (e.g. many calcifiers) are habitat-forming organisms providing shelter, food and nursery functions to many marine species, including commercially important fish species. They also contribute to coastal protection, leisure, recreation and other cultural benefits. Nutrient cycling e.g. changes in N-fixation [198,298], or changes in bioturbator and bio-irrigator communities will also change the fundamental processes within ecosystems [103].

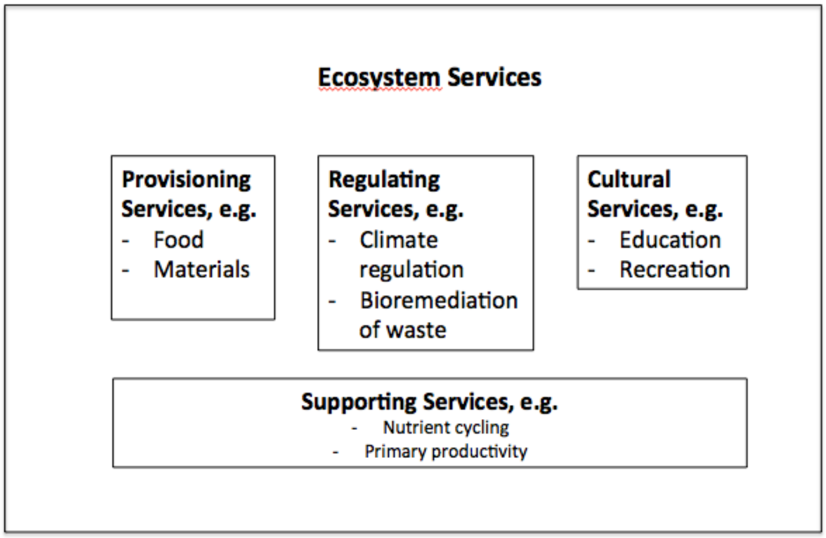
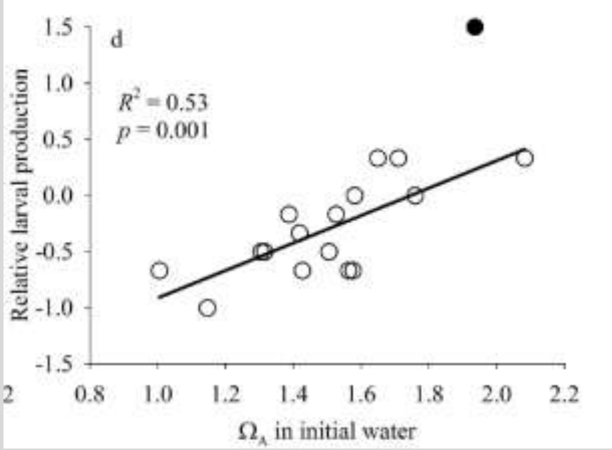


Figure 5.18. Simplified summary of ecosystem services with selected examples given

Provisioning services - Evidence supporting the impacts on provisioning services is variable. Molluscs and crustaceans harvested for food are likely to be affected as they have calcareous shells and exoskeletons. Non-experimental evidence of the impact of OA on molluscs has been reported at sites along the Pacific North West of the USA where the failure of oyster reproduction in hatcheries has been attributed to high levels of CO_2 in the water that upwells along that coast [299,300] (Box 5.2) Impacts such as these may have different implications depending upon their location. For example, small island states that are reliant upon shellfish aquaculture for export and for protein intake would be particularly vulnerable to ocean acidification in this instance [301]. However, adaptation of organisms may also be possible, as seems to be the case for molluscs reportedly thriving in naturally CO_2 enriched waters (e.g. Kiel Fjord [165]). Some other species may be indirectly impacted by ocean acidification by changes in their food chain and habitat. Examples include finfish, [302] such as haddock, which feed on calcifying organisms like echinoderms. It is also important to consider the national impacts of altered provisional services

Box 5.2 Impact of ocean acidification on oyster hatcheries

Due to the naturally low and variable pH of upwelled water off the north west coast of the U.S.A., there is strong evidence that additional acidification due to anthropogenic CO2 is already having biological impacts in that region – where carbonate saturation values are now at levels projected for elsewhere 50-100 years in the future. Thus established oyster hatcheries in Oregon and Washington have increasingly suffered high larval mortalities (up to 80%) since 2006, threatening the viability of an industry with total economic value of around $280 million per year [305]. Barton et al. [300] documented the variable carbonate chemistry and pH of the hatchery water due to periodic upwelling events, relating that variability to the success of larval production and mid-stage growth cohorts of the Pacific oyster *Crassostrea gigas*. The oyster hatcheries have now adapted their working practices so that they avoid using very low pH seawaters by recirculating their seawater systems during upwelling events. With these new practices, the northwest oyster hatcheries are producing close to full capacity again.



Relationship between aragonite saturation state (ΩA) in incoming seawater and relative larval production at the Whiskey Creek oyster hatchery, Oregon. Negative production values indicate reduction in total biomass, due to mortality exceeding growth. From [300].

Regulating services - This includes coastal defense and carbon storage. Many marine communities (e.g. tropical coral reefs, mangroves, seagrass meadows and bivalve beds) can dissipate the energy in waves reaching the coast, influence sedimentation rates and affect levels of erosion at the coast [303,304]. Changes in these communities resulting from ocean acidification will therefore affect their ability to protect the coast. In addition, while potential impacts of ocean acidification on corals and bivalves may be negative, this may not be true for seagrasses, which may benefit from higher levels of CO_2 [183] in the water and may therefore afford greater protection of the coast.

Cultural services - The impact of ocean acidification on cultural ecosystem services is particularly difficult to assess. While impacts to tourism, leisure and recreation can be partially quantified, e.g. through potential degradation to reefs attracting less tourism due to dead coral and through decreased ancillary biodiversity, many cultural services, such as spiritual enrichment and aesthetic appreciation, are intangible in nature and the role of biodiversity in these services is unclear. Nevertheless, where marine species are important to, for example, people's heritage and identity (e.g. in some native Australian communities) any loss of these species may lead to further erosion of their heritage and identity. Understanding the impacts of ocean acidification on tourism, leisure and recreation is also challenging, and more research is required to quantify this.

5.4.2 Economic/livelihood impact

Assessing the impacts of ocean acidification on economic welfare requires that the full impact pathway is understood and modeled. This demands the coupling or integration of models that explain each step in the pathway linking (1) socio-economic activities, CO_2 emissions, ocean acidification, (2) impacts on marine ecosystems, (3) changes in the provision of ecosystem services, and finally (4) impacts on human welfare.

Reviewing the existing economic literature on ocean acidification, only a partial set of the potentially impacted ecosystem services have been assessed, with a focus on the direct use values that can be more easily addressed. Of the thirteen studies reviewed in Table 5.1 only five provide monetary estimates of the costs of ocean acidification. Three of these are for impacts on mollusc fisheries (two for the US and one global estimate); one covers impacts on fisheries and carbon storage; and one is for impacts on coral reef services. Central estimates from each study are presented in Table 5.1 and standardized to annual values in the terminal year of each analysis in US$ at 2010 price levels. From the limited information that is currently available, it appears that impacts to tropical coral reef services dominate, so these are examined in more detail below.

The economic impacts of ocean acidification on the fisheries industry are relatively understudied. However, models suggest that there may be a substantial reduction in potential fisheries catch in more acidic waters [306]. This would impact upon quantity, quality and predictability of future catches [307]. It is also important to consider projected impacts upon different communities i.e. indigenous communities as well as global markets. Coastal indigenous peoples catch large quantities of marine species, which may be consumed, or traded with some inland groups in exchange for other indigenous foods like plants, berries, and terrestrial mammals. This may also differ regionally, and it could be that coastal communities in the Arctic are likely to be affected disproportionally by ocean acidification due to the rapid environmental changes towards higher latitudes. Urgent research is thus needed to understand likely impacts in multiple coastal communities.

The only study to provide values of the global economic impact of ocean acidification on tropical coral reefs estimates the potential annual value of lost ecosystem services to be up to ~US$1000 billion by 2100 [308]. The value varies across scenarios due to (1) differing projected rates of CO_2 emissions, ocean acidification and loss of coral cover; and (2) differing rates of population and income growth that determine the value of coral reef services per unit area of coral cover. The results show that the annual economic impact (loss of coral reef service value) escalates rapidly over time, essentially because the scenarios have high economic growth in countries with coral reefs, and because demand for coral reef services increases more than proportionately with income. Nonetheless, the annual value of foregone ecosystem services from coral reefs in 2100 is still only estimated to be a small fraction of total global income (0.14% or US$ 870 billion in 2100; 2000 price levels; Special Report on Emissions Scenario A1B based on rapid and integrated world economic growth).

Table 5.1. *Summary of studies that examine the economic impacts of ocean acidification. Brander et al.* [308]

Study	**Impacts**	**Geographic scope**	**Emissions scenario**	**Period of analysis**	**Welfare measure**[1]	**Annual value (US$; billions)**[2]
Armstrong et al. (2012) [309]	Fisheries	Norway	pH decrease 0.5	2010 – 2110	Revenue	0.01
	Carbon storage	Norway	pH decrease 0.5	2010 – 2110	Damage Cost	3
Brander et al. (2012) [310]	Coral reefs	Global	SRES A1B	2000 - 2100	Mixed	1,093
Cheung et al. (2011) [306]	Fish and invertebrates	N-E Atlantic	SRES A1B	2005 - 2050	-	-
Cooley & Doney (2009) [311]	Molluscs	United States	IPCC A1F1	2007 - 2060	Revenue	0.07
Cooley et al. (2012) [301]	Molluscs	Global	CCSM3	2010 - 2060	-	-
Finnoff (2010) [312]	Fisheries; non-use values	Baring Sea	-	-	-	-
Harrould-Kolieb et al. (2009) [313]	Coral reefs; fisheries	Global	SRES A1B	2009 - 2050	-	-
Hilmi et al. (2012) [314]	All	Global	-	-	-	-
Kite-Powell (2009) [315]	Coral reefs; fisheries	Global	IS92a	-	-	-
Moore (2011) [316]	Molluscs	United States	RCP8.5; RCP6	2010 - 2100	CV	0.31
Narita et al. (2012) [317]	Molluscs	Global	IS92a	2000 - 2100	CS, PS	139
Rodrigues et al. (2013) [318]	Use and non-use values	Mediterranean	-	-	-	-
Sumaila et al. (2011) [307]	Capture fisheries	Global	-	-	-	-

[1] CV: compensating variation; CS: consumer surplus; PS: producer surplus

[2] Impact estimates are standardised to annual values for the terminal year in each analysis (i.e., 2060 for Cooley and Doney [311] and 2100 otherwise) in US$ 2010 price level

The estimated impacts are, however, considered to be partial since the underlying value data is largely focused on recreational values and includes limited information on the value of other services such as coastal protection or non-use values for biodiversity. Results of a sensitivity analysis show that the estimated impact is highly uncertain, with a confidence interval spanning one order of magnitude. It is important to note that other threats to the health of coral reefs and the provision of reef services are not included (e.g. over fishing, sedimentation, eutrophication, sea level and temperature rise) [319].

5.4.3 Projected impacts on ocean biogeochemical cycles

In the previous section, the impact of ocean acidification upon ecosystem services and human livelihoods was discussed. However, ocean acidification also has the potential to affect major biogeochemical cycles [320] and be of global concern. In assessing the potential impacts of ocean acidification on biogeochemical cycles it is important to recognise that ocean acidification impacts do not occur in isolation, but will occur in conjunction with other stressors including ocean warming, and potentially increased UV radiation, and these changes might significantly modulate future impacts [321].

Acidification has the potential to modify the ocean's biogeochemical cycles in a number of ways, which could alter the climate. We use the term biogeochemical climate feedback to denote biogeochemical processes in the ocean that could either enhance (positive feedback) or reduce (negative feedback) future global warming due to rising greenhouse gases. To investigate these feedbacks, we primarily focus on biogeochemical processes in the ocean that are impacted by ocean acidification, and that can alter ocean uptake and storage of carbon. To help simplify the discussion of the potential impacts of ocean acidification on biogeochemical cycles, a summary is provided in Table 5.2, and some processes that 1) alter **biological production** in the photic zone (where light penetrates), and 2) alter the **remineralisation** (or breakdown) of sinking particulate organic and inorganic carbon are discussed in more detail below.

Key Messages: 5.4.3

1. Rising CO_2 will affect net primary productivity, alter nitrogen and carbon ratios in exported particulate matter, and decrease iron bioavailability

2. Ocean acidification could decrease particulate organic carbon export to the deep ocean

3. Net effect of ocean acidification on ocean productivity and carbon storage is uncertain

4. Decreased dimethyl sulphide (DMS) production could lead to exacerbated global warming

Biological production

Rising CO_2 concentrations in the upper ocean have the potential to affect biological production in several ways:

- Increase net primary productivity and Particulate Organic Carbon (POC) production by making photosynthesis more efficient [202,209]. However, increased vertical stratification of the upper ocean is likely to reduce nutrient supplies to the euphotic zone which may counteract potential effects of rising $p\text{CO}_2$ on phytoplankton production in the open ocean [322].
- Alter the stoichiometric nitrogen to carbon ratio in exported particulate organic matter (POM), as observed in mesocosm experiments by Riebesell et al. [323] and Bellerby et al., [324]: C/N ratio increased from 6.0 at 350 µatm to 8.0 at ~1050 µatm. Assuming sufficient supplies of N and other essential nutrients, this could increase the storage of carbon in the ocean [325].

Table 5.2. Summary of likely main effects of future ocean acidification on global-scale biogeochemical processes and feedbacks to the climate system (primarily by increasing or decreasing atmospheric CO_2) based on Table 12.1 of Gehlen et al. [320] and the ~70 references cited in that paper. Note that: i) this table focuses on water column effects in the open ocean; ii) all processes except (1) and (5) involve indirect effects, mediated by marine biota (mostly phytoplankton, and bacteria); iii) information for processes (7) and (8) is based on Hopkins et al. [335] and Six et al. [336]; and iv) information for (9) based on references discussed in text. Level of understanding: H, high; M, medium; L, low.

Process	Effect of future OA	Feedback	Magnitude	Level of under-standing
1. Ocean's ability to buffer atmospheric CO_2 levels	Decreased ocean uptake capacity	+ ve	Large	H
2. Photo-synthesis	Enhanced biological production and organic export from upper ocean	– ve	Medium	M
3. C:N ratio of biomass	Increased C:N ratio, affecting food quality and carbon export	– ve	Small to medium	L
4. Calcification	Overall decrease in biocalcification (but not all species/strains?)	– ve	Small to medium	L/M
5. Carbonate dissolution	Increased $CaCO_3$ dissolution in particles and sediments, increasing ocean alkalinity	– ve	Small in short-term; large in long-term	M
6. Ballast effect (sinking particles)	Decreased $CaCO_3$ production will reduce organic matter export	+ ve	Small to medium	L
7. Dimethyl suphide (DMS)	Reduced DMS production	+ ve*	Medium?	L
8. Organo-halogens	Contradictory evidence: both enhancement and reduction may occur	?	Small?	L
9. Nitrogen fixation	Contradictory evidence: both enhancement and reduction may occur	?	Small?	L
10. Oxygenation	Shallower remineralization increases O_2 demand; expansion of low O_2 regions	+ ve	Medium	L
11. Nitrification	Reduced nitrification	?	Small	L
12. Nitrous oxide production	Decreased O_2 levels will increase N_2O production	+ ve	Medium	L

*feedback via cloud formation

- Affect dinitrogen (N_2) fixation by cyanobacteria, which could also alter primary production in nitrogen-limited areas. Initial experiments showed that *Trichodesmium* may increase its nitrogen fixation under elevated CO_2 [326], however, there were strain-specific differences [327] and other cyanobacteria did not respond similarly[328,329]. Under realistic (low Fe) nutrient levels, low pH may reduce nitrogen fixation by *Trichodesmium* through effects on iron uptake [330].
- Impede the ability of organisms to calcify [5]. This is anticipated to reduce the production of calcium carbonate.
- Decrease the bioavailability of dissolved iron (Fe) to some phytoplankton species.. Acidification of seawater decreases the Fe uptake rate of diatoms and coccolithophores [331].

Remineralisation (breakdown) of particulate material

Dissolution of $CaCO_3$ is predicted to increase in response to projected declines in saturation state [11]. Most of the exported organic carbon is broken down in the upper 1000 m, but roughly 10% escapes to the deep ocean, where it is broken down in the water column or buried in sediments and sequestered from the atmosphere on millennial timescales [332]. The analysis of particulate inorganic and organic carbon (PIC and POC) fluxes to water depths greater than 1000 m suggests a close association between these fluxes [47]. Armstrong et al. [193] proposed that $CaCO_3$ acts as "'ballast" for transporting POC at the surface to deeper waters, thereby increasing its sinking speed. It is also hypothesized that the association between $CaCO_3$ and POC might protect the latter from bacterial degradation. If deep-water POC fluxes are controlled by $CaCO_3$, then a decrease in $CaCO_3$ production would reduce POC transport to the deep ocean. POC would break down at shallower depths, and the overall efficiency of the biological pump would decrease, resulting in reduced carbon storage in the ocean and seabed, thereby increasing atmospheric CO_2. There is also evidence from different regions that bacterial exoenzyme activity may increase under elevated CO_2 [333,334]. One potential outcome is an increase in the breakdown of organic carbon in surface waters, potentially decreasing the biological pump and carbon storage in the ocean.

Looking to the end of the century, Earth System Model (ESM) [337] can be used to explore the potential consequences of ocean acidification on the marine biogeochemical cycles identified in Table 5.2, and identify that key biogeochemical parameters in the ocean will be significantly altered [337]. These include aragonite and calcite saturation state, export production, and interior dissolved oxygen concentrations. The general consensus of multi-model climate projections is a reduction in primary production and export production with global warming [338,339] although there are important regional differences between model projections. Where ocean acidification impacts could be significant is on the POC and PIC export from the upper ocean [337,340]. This would affect the flow of energy through ecosystems, and could have significant impacts on marine ecosystem productivity and biodiversity.

In addition, large changes in PIC and POC export could significantly alter ocean interior oxygen levels. Oceanic oxygen levels are expected to decline under global warming [341,342], and the latest ESMs project a small decrease in the total ocean inventory of dissolved oxygen (2% to 4%) by the end of 2100 [338]. However, the projections vary regionally, and the total volume of hypoxic and suboxic waters remain relatively unchanged by the end of 2100. The decline in oxygen with rising CO_2 could also have important consequences for marine organisms with high metabolic rates. Global warming, lower oxygen and higher CO_2 levels thus represent physiological stresses for marine aerobic organisms that may act synergistically with ocean acidification [264].

Other gases - While CO_2 is the most important greenhouse gas modulated by the ocean, other greenhouses gases may also be altered by ocean acidification. These include methane (CH_4) and nitrous oxide (N_2O), as their production in the ocean is linked to the breakdown of organic matter in low oxygen water [343,344]. Declining oxygen levels should be associated with increased production of both these gases [345,346], but it is expected that the impact of increased production of CH_4 and N_2O would be less than the projected impacts of increased CO_2 [337]. However, increased warming could also potentially destabilise methane hydrates stored in sediments along continental margins, leading to additional release of CH_4 [347].

The potential effects of increasing anthropogenic CO_2 on trace gas production in the oceans are poorly understood. These trace gases include climatically important gases, such as dimethyl sulphide (DMS), which can alter cloud properties. DMS is a gaseous sulphur compound produced by marine biota in surface seawater [348] and provides 90% of the biogenic sulfur in the marine atmosphere [349]. Modelling studies vary substantially in their predictions of the change in DMS emissions with climate change; studies for polar waters suggest increases in DMS emission ranging from 30% to more than 150% by 2100 [350-352], but elevated CO_2 predictions in isolation of other environmental change suggest a significant decrease in future concentration of DMS [335, 336] (Figure 5.19). When combined in Earth System Models to simulate future climate change, decreased DMS production could exacerbate global warming [336]. However, DMS production responses measured to date are variable, and the sensitivity of the climate system to such changes is uncertain, and may be low[353]. Thus full understanding of the combined global warming and ocean acidification impact on marine DMS and other trace gas production needs further study to determine its importance.

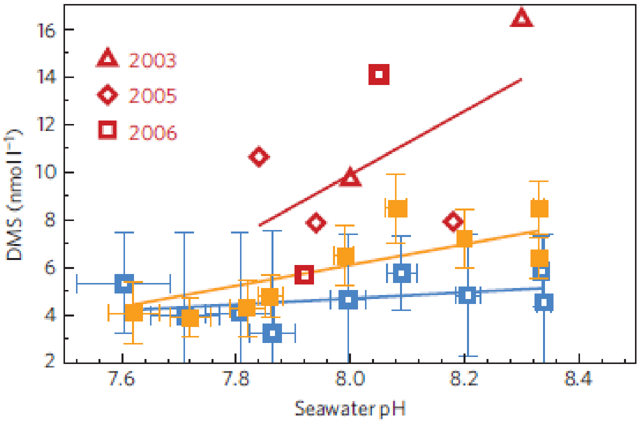


Figure 5.19. Relationship between DMS concentration and pH based on data from mesocosm experiments. Measurements of DMS and seawater pH are averaged from the mid-phase of Svalbard experiments (orange) and over the entire experiment (blue). Red denotes measurements from Norwegian mesocosm experiments from three different years. Source: [336].

1. Seibel BA, Walsh PJ (2001) Potential impacts of CO2 injection on deep-sea biota. Science 294: 64-65.
2. Esbaugh AJ, Heuer R, Grosell M (2012) Impacts of ocean acidification on respiratory gas exchange and acid-base balance in a marine teleost, Opsanus beta. Journal of Comparative Physiology B-Biochemical Systemic and Environmental Physiology 182: 921-934.
3. Strobel A, Bennecke S, Leo E, Mintenbeck K, Poertner HO, et al. (2012) Metabolic shifts in the Antarctic fish Notothenia rossii in response to rising temperature and PCO2. Frontiers in Zoology 9.
4. Stumpp M, Hu M, Casties I, Saborowski R, Bleich M, et al. (2013) Digestion in sea urchin larvae impaired under ocean acidification. Nature Climate Change 3: 1044-1049.
5. Fabry V, Seibel B, Feely RA (2008) Impacts of ocean acidification on marine fauna and ecosystem processes. Journal of Marine Research 65: 414-432.
6. Hand SC (1992) Metabolic dormancy in aquatic invertebrates. In: Gilles R, editor. Advances in Comparative and Environmental Physiology. Heidelberg: Springer-Verlag.
7. Seibel BA, Walsh PJ (2003) Biological impacts of deep-sea carbon dioxide injection inferred from indices of physiological performance. Journal of Experimental Biology 206: 641-650.
8. Barry JP, Widdicombe S, Hall-Spencer JM (2011) Effects of ocean acidification on marine biodiversity and ecosystem function. In: Gattuso JP, L. H, editors. Ocean Acidification. Oxford: Oxford University Press.
9. Gattuso JP, Hansson L (2011) Ocean Acidification. Oxford: Oxford University Press.
10. Dickson AG (2010) The carbon dioxide system in seawater: equilibrium chemistry and measurements. In: Riebesell U, Fabry VJ, L. H, Gattuso JP, editors. Guide to best practices for ocean acidifcation research and data reporting. Luxenbourg: European Union. pp. 17-40.
11. Orr JC, Fabry VJ, Aumont O, Bopp L, Doney SC, et al. (2005) Anthropogenic ocean acidification over the twenty-first century and its impact on calcifying organisms. Nature 437: 681-686.
12. Tambutté S, Holcomb M, Ferrier-Pagès C, Reynaud S, Tambutté É, et al. (2011) Coral biomineralization: From the gene to the environment. Journal of Experimental Marine Biology and Ecology 408: 58-78.
13. Erez J, Reynaud S, Silverman J, Schneider K, Allemand D (2011) In: Dubinsky Z, Stambler N, editors. Coral Reefs: an ecosystem in transition.
14. Tambutte E, Tambutte S, Segonds N, Zoccola D, Venn A, et al. (2012) Calcein labelling and electrophysiology: insights on coral tissue permeability and calcification. Proceedings of the Royal Society B-Biological Sciences 279: 19-27.
15. Rodolfo-Metalpa R, Houlbrèque F, Tambutté É, Boisson F, Baggini C, et al. (2011) Coral and mollusc resistance to ocean acidification adversely affected by warming. Nature Climate Change 1: 1-5.
16. Ries J (2011) Acid ocean cover up. Nature Climate Change 1: 294-295.
17. Venn A, Tambutte E, Holcomb M, Allemand D, Tambutte S (2011) Live tissue imaging shows reef corals elevate pH under their calcifying tissue relative to seawater. PLoS ONE 6: e20013.
18. McCulloch M, Falter J, Trotter J, Montagna P (2012) Coral resilience to ocean acidification and global warming through pH up-regulation. Nature Climate Change 2: 623-633.
19. Venn AA, Tambutte E, Holcomb M, Laurent J, Allemand D, et al. (2013) Impact of seawater acidification on pH at the tissue-skeleton interface and calcification in reef corals. Proceedings of the National Academy of Sciences of the United States of America 110: 1634-1639.
20. Cohen AL, Holcomb M (2009) Why corals care about ocean acidification: Uncovering the mechanism. 22: 118-127.
21. Vidal-Dupiol J, Zoccola D, Tambutte E, Grunau C, Cosseau C, et al. (2013) Genes Related to Ion-Transport and Energy Production Are Upregulated in Response to CO2-Driven pH Decrease in Corals: New Insights from Transcriptome Analysis. Plos One 8.
22. Kaniewska P, Campbell PR, Kline DI, Rodriguez-Lanetty M, Miller DJ, et al. (2012) Major cellular and physiological impacts of ocean acidification on a reef building coral. PLoS ONE 7: e34659-e34659.

23. Pechenik JA (1999) On the advantages and disadvantages of larval stages in benthic marine invertebrate life cycles. Marine Ecology Progress Series 177: 269-297.
24. Byrne M (2012) Global change ecotoxicology: Identification of early life history bottlenecks in marine invertebrates, variable species responses and variable experimental approaches. Marine Environmental Research 76: 3-15.
25. Havenhand J, Dupont S, Quinn GP (2010) Designing ocean acidification experiments to maximise inference. In: Riebesell U, Fabry VJ, Hansson L, Gattuso JP, editors. Guide to best practices for ocean acidification research and data reporting. Luxembourg: European Union. pp. 67-80.
26. Lewis C, Clemow K, Holt WV (2013) Metal contamination increases the sensitivity of larvae but not gametes to ocean acidification in the polychaete Pomatoceros lamarckii (Quatrefages). Marine Biology 160: 2089-2101.
27. Reuter K, Lotterhos KE, Crim RN, Thompson CA, Harley CDG (2010) Elevated pCO2 increases sperm limitation and risk of polyspermy in the red sea urchin Strongylocentrotus franciscanus. Global Change Biology.
28. Evans JP, Marshall DJ (2005) Male-by-female interactions influence fertilization success and mediate the benefits of polyandry in the sea urchin Heliocidaris erythrogramma. Evolution 59: 106-112.
29. Palumbi SR (1999) All males are not created equal: Fertility differences depend on gamete recognition polymorphisms in sea urchins. Proceedings of the National Academy of Sciences of the United States of America 96: 12632-12637.
30. Hendriks IE, Duarte CM, Álvarez M (2010) Vulnerability of marine biodiversity to ocean acidification: A meta-analysis. Estuarine, Coastal and Shelf Science 86: 157-164.
31. Wittmann AC, Portner H-O (2013) Sensitivities of extant animal taxa to ocean acidification. Nature Climate Change 3: 995-1001.
32. Kroeker KJ, Kordas RL, Crim R, Hendriks IE, Ramajo L, et al. (2013) Impacts of ocean acidification on marine organisms: quantifying sensitivities and interaction with warming. Global Change Biology 19: 1884-1896.
33. Byrne M, Soars N, Selvakumaraswamy P, Dworjanyn SA, Davis AR (2010) Sea urchin fertilization in a warm, acidified and high pCO(2) ocean across a range of sperm densities. Marine Environmental Research 69: 234-239.
34. Byrne M, Soars NA, Ho MA, Wong E, McElroy D, et al. (2010) Fertilization in a suite of coastal marine invertebrates from SE Australia is robust to near-future ocean warming and acidification. Marine Biology 157: 2061-2069.
35. Ho MA, Price C, King CK, Virtue P, Byrne M (2013) Effects of ocean warming and acidification on fertilization in the Antarctic echinoid Sterechinus neumayeri across a range of sperm concentrations. Marine Environmental Research 90: 136-141.
36. Havenhand JN, Buttler F-R, Thorndyke MC, Williamson JE (2008) Near-future levels of ocean acidification reduce fertilization success in a sea urchin. Current Biology 18: R651-R652.
37. Havenhand JN, Schlegel P (2009) Near-future levels of ocean acidification do not affect sperm motility and fertilization kinetics in the oyster Crassostrea gigas. Biogeosciences 6: 3009-3015.
38. Schlegel P, Havenhand JN, Gillings MR, Williamson JE (2012) Individual Variability in Reproductive Success Determines Winners and Losers under Ocean Acidification: A Case Study with Sea Urchins. Plos One 7.
39. Foo SA, Dworjanyn SA, Poore AGB, Byrne M (2012) Adaptive capacity of the habitat modifying sea urchin Centrostephanus rodgersii to ocean warming and ocean acidification: performance of early embryos. Plos One 7.
40. Albright R, Mason B (2013) Projected Near-Future Levels of Temperature and pCO2 Reduce Coral Fertilization Success. PLoS ONE 8: 1-8.
41. Caldwell GS, Fitzer S, Gillespie CS, Pickavance G, Turnbull E, et al. (2011) Ocean acidification takes sperm back in time. Invertebrate Reproduction & Development 55: 217-221.
42. Mita M, Hino A, Yasumasu I (1984) Effect of temperature on interaction between eggs and spermatozoa of sea-urchin. Biological Bulletin 166: 68-77.
43. Kupriyanova EK, Havenhand JN (2005) Effects of temperature on sperm swimming behaviour, respiration and fertilization success in the serpulid polychaete, Galeolaria caespitosa (Annelida : Serpulidae). Invertebrate Reproduction & Development 48: 7-17.
44. Byrne M, Ho M, Selvakumaraswamy P, Nguyen HD, Dworjanyn SA, et al. (2009) Temperature, but not pH, compromises sea urchin fertilization and early development under near-future climate change scenarios. Proceedings of the Royal Society B-Biological Sciences 276: 1883-1888.
45. Ericson Ja, Lamare MD, Morley Sa, Barker M (2010) The response of two ecologically important Antarctic invertebrates (Sterechinus neumayeri and Parborlasia corrugatus) to reduced seawater pH: effects on fertilisation and embryonic development. Marine Biology: 2689-2702.
46. Byrne M, Ho M, Wong E, Soars NA, Selvakumaraswamy P, et al. (2011) Unshelled abalone and corrupted urchins: development of marine calcifiers in a changing ocean. Proceedings of the Royal Society B-Biological Sciences 278: 2376-2383.
47. Kurihara H, Ishimatsu A (2008) Effects of high CO_2 seawater on the copepod (*Acartia tsuensis*) through all life stages and subsequent generations. Marine pollution bulletin 56: 1086-1090.
48. Dupont S, Ortega-Martínez O, Thorndyke MC (2010) Impact of near-future ocean acidification on echinoderms. Ecotoxicology (London, England) 19: 449-462.
49. Gazeau F, Gattuso J-P, Dawber C, Pronker aE, Peene F, et al. (2010) Effect of ocean acidification on the early life stages of the blue mussel *Mytilus edulis*. Biogeosciences 7: 2051-2060.
50. Hofmann GE, Barry JP, Edmunds PJ, Gates RD, Hutchins DA, et al. (2010) The Effect of Ocean Acidification on Calcifying Organisms in Marine Ecosystems: An Organism-to-Ecosystem Perspective. Annual Review of Ecology, Evolution, and Systematics 41: 127-147.
51. Byrne M, Przeslawski R (2013) Multistressor impacts of warming and acidification of the ocean on marine invertebrates' life histories. Integrative and Comparative Biology 53: 582-596.
52. Dupont S, Havenhand J, Thorndyke W, Peck L, Thorndyke M (2008) Near-future level of CO2-driven ocean acidification radically affects larval survival and development in the brittlestar Ophiothrix fragilis. Marine Ecology Progress Series 373: 285-294.
53. Parker LM, Ross P, O'Connor W (2010) Comparing the effect of elevated pCO_2 and temperature on the fertilization and early development of two species of oysters. Marine Biology 11: 2435-2452.
54. Parker LM, Ross PM, O'Connor WA, Borysko L, Raftos DA, et al. (2012) Adult exposure influences offspring response to ocean acidification in oysters. Global Change Biology 18: 82-92.
55. Byrne M (2011) Impact of ocean warming and ocean acidification on marine invertebrate life history stages: vulnerabilities and potential for persistence in a changing ocean. In: Gibson RN, Atkinson RJA, Gordon JDM, editors. Oceanography and Marine Biology: an Annual Review, Vol 49. pp. 1-42.
56. Barros P, Sobral P, Range P, Chicharo L, Matias D (2013) Effects of sea-water acidification on fertilization and larval development of the oyster Crassostrea gigas. Journal of Experimental Marine Biology and Ecology 440: 200-206.

57. Stumpp M, Wren J, Melzner F, Thorndyke MC, Dupont ST (2011) CO2 induced seawater acidification impacts sea urchin larval development I: Elevated metabolic rates decrease scope for growth and induce developmental delay. Comparative Biochemistry and Physiology a-Molecular & Integrative Physiology 160: 331-340.
58. Stumpp M, Hu MY, Melzner F, Gutowska MA, Dorey N, et al. (2012) Acidified seawater impacts sea urchin larvae pH regulatory systems relevant for calcification. Proceedings of the National Academy of Sciences of the United States of America 109: 18192-18197.
59. Byrne M, Lamare M, Winter D, Dworjanyn SA, Uthicke S (2013) The stunting effect of a high CO2 ocean on calcification and development in sea urchin larvae, a synthesis from the tropics to the poles. Philos Trans R Soc Lond B Biol Sci 368: 20120439.
60. Sheppard Brennand H, Soars N, Dworjanyn Sa, Davis AR, Byrne M (2010) Impact of ocean warming and ocean acidification on larval development and calcification in the sea urchin *Tripneustes gratilla.* PloS one 5: e11372.
61. Walther K, Sartoris F, Pörtner H (2011) Impacts of temperature and acidification on larval calcium incorporation of the spider crab *Hyas araneus* from different latitudes (54° vs. 79°N). Marine Biology In press: 1-11.
62. Byrne M, Ho MA, Koleits L, Price C, King CK, et al. (2013) Vulnerability of the calcifying larval stage of the Antarctic sea urchin Sterechinus neumayeri to near-future ocean acidification and warming. Global Change Biology 19: 2264-2275.
63. Gianguzza P, Visconti G, Gianguzza F, Vizzini S, Sara G, et al. (2014) Temperature modulates the response of the thermophilous sea urchin Arbacia lixula early life stages to CO2-driven acidification. Mar Environ Res 93: 70-77.
64. Dupont S (2010) Near future ocean acidification increases growth rate of the lecithotrophic larvae and juveniles of the sea star Crossaster papposus. Journal of Experimental ….
65. Byrne M, Gonzalez-Bernat M, Doo S, Foo S, Soars N, et al. (2013) Effects of ocean warming and acidification on embryos and non-calcifying larvae of the invasive sea star Patiriella regularis. Marine Ecology Progress Series 473: 235-+.
66. Chua CM, Leggat W, Moya A, Baird AH (2013) Temperature affects the early life history stages of corals more than near future ocean acidification. Marine Ecology Progress Series 475: 85-92.
67. Gonzalez-Bernat MJ, Lamare M, Barker M (2013) Effects of reduced seawater pH on fertilisation, embryogenesis and larval development in the Antarctic seastar Odontaster validus. Polar Biology 36: 235-247.
68. Nguyen HD, Doo SS, Soars NA, Byrne A (2012) Noncalcifying larvae in a changing ocean: warming, not acidification/hypercapnia, is the dominant stressor on development of the sea star Meridiastra calcar. Global Change Biology 18: 2466-2476.
69. Walther K, Anger K, Pörtner HO (2010) Effects of ocean acidification and warming on the larval development of the spider crab Hyas araneus from different latitudes (54 ° vs . 79 ° N). Marine Ecology Progress Series 417: 159-170.
70. Pansch C, Schlegel P, Havenhand J (2013) Larval development of the barnacle Amphibalanus improvisus responds variably but robustly to near-future ocean acidification. Ices Journal of Marine Science 70: 805-811.
71. Pansch C, Nasrolahi A, Appelhans YS, Wahl M (2012) Impacts of ocean warming and acidification on the larval development of the barnacle Amphibalanus improvisus. Journal of Experimental Marine Biology and Ecology 420: 48-55.
72. Arnberg M, Calosi P, Spicer JI, Tandberg AHS, Nilsen M, et al. (2013) Elevated temperature elicits greater effects than decreased pH on the development, feeding and metabolism of northern shrimp (Pandalus borealis) larvae. Marine Biology 160: 2037-2048.
73. Doropoulos C, Diaz-Pulido G (2013) High CO2 reduces the settlement of a spawning coral on three common species of crustose coralline algae. Marine Ecology Progress Series 475: 93-99.
74. Albright R, Mason B, Langdon C (2008) Effect of aragonite saturation state on settlement and post-settlement growth of Porites astreoides larvae. Coral Reefs 27: 485-490.
75. Albright R, Bland C, Gillette P, Serafy JE, Langdon C, et al. (2012) Juvenile growth of the tropical sea urchin Lytechinus variegatus exposed to near-future ocean acidification scenarios. Journal of Experimental Marine Biology and Ecology 426: 12-17.
76. Anlauf H, D'Croz L, O'Dea A (2011) A corrosive concoction: The combined effects of ocean warming and acidification on the early growth of a stony coral are multiplicative. Journal of Experimental Marine Biology and Ecology 397: 13-20.
77. Talmage SC, Gobler CJ (2011) Effects of Elevated Temperature and Carbon Dioxide on the Growth and Survival of Larvae and Juveniles of Three Species of Northwest Atlantic Bivalves. Plos One 6.
78. Wolfe K, Dworjanyn SA, Byrne M (2013) Effects of ocean warming and acidification on survival, growth and skeletal development in the early benthic juvenile sea urchin (Heliocidaris erythrogramma). Global Change Biology 19: 2698-2707.
79. Suwa R, Nojiri Y, Ono T, Shirayama Y (2013) Effects of low pCO2conditions on sea urchin larval size. Marine Ecology 34: 443-450.
80. Thomsen J, Casties I, Pansch C, Koertzinger A, Melzner F (2013) Food availability outweighs ocean acidification effects in juvenile Mytilus edulis: laboratory and field experiments. Global Change Biology 19: 1017-1027.
81. Findlay HS, Kendall MA, Spicer JI, Widdicombe S (2010) Post-larval development of two intertidal barnacles at elevated CO2 and temperature. Marine Biology 157: 725-735.
82. Findlay HS, Kendall Ma, Spicer JI, Widdicombe S (2010) Relative influences of ocean acidification and temperature on intertidal barnacle post-larvae at the northern edge of their geographic distribution. Estuarine, Coastal and Shelf Science 86: 675-682.
83. Poore AGB, Graba-Landry A, Favret M, Brennand HS, Byrne M, et al. (2013) Direct and indirect effects of ocean acidification and warming on a marine plant-herbivore interaction. Oecologia 173: 1113-1124.
84. Briffa M, de la Haye K, Munday PL (2012) High CO2 and marine animal behaviour: Potential mechanisms and ecological consequences. Marine Pollution Bulletin 64: 1519-1528.
85. Munday PL, McCormick MI, Nilsson GE (2012) Impact of global warming and rising CO2 levels on coral reef fishes: what hope for the future? Journal of Experimental Biology 215: 3865-3873.
86. Munday PL, Dixson DL, Donelson JM, Jones GP, Pratchett MS, et al. (2009) Ocean acidification impairs olfactory discrimination and homing ability of a marine fish. Proceedings of the National Academy of Sciences of the United States of America 106: 1848-1852.
87. Dixson DL, Munday PL, Jones GP (2010) Ocean acidification disrupts the innate ability of fish to detect predator olfactory cues. Ecology letters 13: 68-75.
88. Knight K (2014) Ocean acidification will interfere with fish eyes. Journal of Experimental Biology 217: 311-312.
89. Chung WS, Marshall NJ, Watson SA, Munday PL, Nilsson GE (2014) Ocean acidification slows retinal function in a damselfish through interference with GABA(A) receptors. Journal of Experimental Biology 217: 323-326.
90. Simpson SD, Munday PL, Wittenrich ML, Manassa R, Dixson DL, et al. (2011) Ocean acidification erodes crucial auditory behaviour in a marine fish. Biology Letters 7: 917-920.
91. Domenici P, Allan B, McCormick MI, Munday PL (2012) Elevated carbon dioxide affects behavioural lateralization in a coral reef fish. Biology Letters 8: 78-81.

92. Ferrari MCO, Manassa RP, Dixson DL, Munday PL, McCormick MI, et al. (2012) Effects of Ocean Acidification on Learning in Coral Reef Fishes. Plos One 7.
93. Munday PL, Dixson DL, McCormick MI, Meekan M (2010) Replenishment of fish populations is threatened by ocean acidification. Proceedings of the National Academy of Science.
94. Ferrari MCO, Dixson DL, Munday PL, McCormick MI, Meekan MG, et al. (2011) Intrageneric variation in antipredator responses of coral reef fishes affected by ocean acidification: implications for climate change projections on marine communities. Global Change Biology 17: 2980-2986.
95. Cripps IL, Munday PL, McCormick MI (2011) Ocean Acidification Affects Prey Detection by a Predatory Reef Fish. Plos One 6.
96. Ferrari MCO, McCormick MI, Munday PL, Meekan MG, Dixson DL, et al. (2011) Putting prey and predator into the CO2 equation - qualitative and quantitative effects of ocean acidification on predator-prey interactions. Ecology Letters 14: 1143-1148.
97. Devine BM, Munday PL (2013) Habitat preferences of coral-associated fishes are altered by short-term exposure to elevated CO_2. Marine Biology 160: 1955-1962.
98. Devine BM, Munday PL, Jones GP (2012) Homing ability of adult cardinalfish is affected by elevated carbon dioxide. Oecologia 168: 269-276.
99. Munday PL, Pratchett MS, Dixson DL, Donelson JM, Endo GGK, et al. (2013) Elevated CO2 affects the behavior of an ecologically and economically important coral reef fish. Marine Biology 160: 2137-2144.
100. Nilsson GE, Dixson DL, Domenici P, McCormick MI, Sorensen C, et al. (2012) Near-future carbon dioxide levels alter fish behaviour by interfering with neurotransmitter function. Nature Climate Change 2: 201-204.
101. Hamilton TJ, Holcombe A, Tresguerres M (2014) CO2-induced ocean acidification increases anxiety in rockfish via alteration of GABAA receptor functioning. Proc Biol Sci 281: 20132509.
102. Lonnstedt OM, Munday PL, McCormick MI, Ferrari MCO, Chivers DP (2013) Ocean acidification and responses to predators: can sensory redundancy reduce the apparent impacts of elevated CO2 on fish? Ecol Evol 3: 3565-3575.
103. Widdicombe S, Spicer J (2008) Predicting the impact of ocean acidification on benthic biodiversity: What can animal physiology tell us? Journal of Experimental Marine Biology and 366: 187-197.
104. Melzner F, Gutowska MA, Langenbuch M, Dupont S, Lucassen M, et al. (2009) Physiological basis for high CO2 tolerance in marine ectothermic animals: pre-adaptation through lifestyle and ontogeny? Biogeosciences 6: 2313-2331.
105. Munday PL, McCormick MI, Meekan M, Dixson DL, Watson S-A, et al. (2012) Selective mortality associated with variation in CO2 tolerance in a marine fish. Ocean Acidification 1: 1-5.
106. Stentiford GD, Neil DM, Peeler EJ, Shields JD, Small HJ, et al. (2012) Disease will limit future food supply from the global crustacean fishery and aquaculture sectors. Journal of Invertebrate Pathology 110: 141-157.
107. Folstad I, Karter AJ (1992) Parasites, bright males, and the immunocompetence handicap. American Naturalist 139: 603-622.
108. Li C-C, Chen J-C (2008) The immune response of white shrimp Litopenaeus vannamei and its susceptibility to Vibrio alginolyticus under low and high pH stress. Fish & Shellfish Immunology 25: 701-709.
109. Matozzo V, Chinellato A, Munari M, Finos L, Bressan M, et al. (2012) First Evidence of Immunomodulation in Bivalves under Seawater Acidification and Increased Temperature. Plos One 7.
110. Dupont S, Thorndyke M (2012) Relationship between CO2-driven changes in extracellular acid-base balance and cellular immune response in two polar echinoderm species. Journal of Experimental Marine Biology and Ecology 424: 32-37.
111. Hernroth B, Baden S, Thorndyke MC, Dupont S (2011) Immune suppression of the echinoderm Asterias rubens (L.) following long-term ocean acidification. Aquatic toxicology (Amsterdam, Netherlands) 103: 222-224.
112. Harvell CD, Mitchell CE, Ward JR, Altizer S, Dobson AP, et al. (2002) Ecology - Climate warming and disease risks for terrestrial and marine biota. Science 296: 2158-2162.
113. Snieszko SF (1974) Effects of environmental stress on outbreaks of infectious-diseases of fishes. Journal of Fish Biology 6: 197-208.
114. Kroeker KJ, Kordas RL, Crim R, Hendriks IE, Ramajo L, et al. (2013) Impacts of ocean acidification on marine organisms: quantifying sensitivities and interaction with warming. Glob Chang Biol 19: 1884-1896.
115. Hall-Spencer JM, Rodolfo-Metalpa R, Martin S, Ransome E, Fine M, et al. (2008) Volcanic carbon dioxide vents show ecosystem effects of ocean acidification. Nature 454: 96-99.
116. Fabricius KE, Langdon C, Uthicke S, Humphrey C, Noonan S, et al. (2011) Losers and winners in coral reefs acclimatized to elevated carbon dioxide concentrations. Nature Climate Change 1: 165-169.
117. Whiteley NM (2011) Physiological and ecological responses of crustaceans to ocean acidification. Marine Ecology Progress Series 430: 257-271.
118. Hendriks IE, Duarte C, Álvarez M (2010) Vulnerability of marine biodiversity to ocean acidification: A meta-analysis. Estuarine, Coastal and Shelf Science 86: 157-164.
119. Hofmann GE, Smith JE, Johnson KS, Send U, Levin LA, et al. (2011) High-Frequency Dynamics of Ocean pH: A Multi-Ecosystem Comparison. Plos One 6.
120. Milazzo M, Rodolfo-Metalpa R, Chan VB, Fine M, Alessi C, et al. (2014) Ocean acidification impairs vermetid reef recruitment. Sci Rep 4: 4189.
121. Reaka-Kudla ML (1997) Global biodiversity of coral reefs: a comparison with rainforests. In: Reaka-Kudla ML, wilson DE, editors. Biodiversity II: Understanding and Protecting Our Biological Resources: Joseph Henry Press.
122. Reaka-Kudla ML (2001) Known and unknown biodiversity, risk of extinction and conservation strategy in the sea. Waters in Peril: 19-33.
123. Dubinsky Z, Stambler N (2011) Coral Reefs: an ecosystem in transition.; Dubinsky Z, Stambler N, editors: Springer.
124. Rogers AD (1999) The biology of Lophelia pertusa (LINNAEUS 1758) and other deep-water reef-forming corals and impacts from human activities. International Review of Hydrobiology 84: 315-406.
125. Freiwald A, Fosså H, Grehan A, Koslow T, Roberts JM Cold-water coral reefs: out of sight-no longer out of mind. 2004 Cambridge, UK
126. Roberts JM, Wheeler A, Freiwald A, Cairns SD (2009) Cold-Water Corals: The Biology and Geology of Deep-Sea Coral Habitats: Cambridge University Press.
127. Findlay HS, Artioli Y, Navas JM, Hennige SJ, Wicks LC, et al. (2013) Tidal downwelling and implications for the carbon biogeochemistry of cold-water corals in relation to future ocean acidification and warming. Global Change Biology 19: 2708-2719.
128. Findlay HS, Hennige SJ, Wicks LC, Navas JM, Woodward EMS, et al. (2014) Fine-scale nutrient and carbonate system dynamics around cold-water coral reefs in the northeast Atlantic. Scientific Reports 4.

129. Roberts JM, Wheeler AJ, Freiwald A (2006) Reefs of the deep: the biology and geology of cold-water coral ecosystems. Science 312: 543-547.

130. Fosså H, Kutti T (2010) Impacts of human activities on benthic habitats. . Arctic Biodiversity Trends Selected indicators of change. Akureyri, Iceland.: CAFF International Secretariat, .

131. Henry L, Navas JM, Hennige S, Wicks LC, Roberts JM (2013) Shark spawning grounds on cold-water coral reefs: a compelling case for protection of vulnerable marine ecosystems. Biological Conservation 161: 67-70.

132. Lunden JJ, Georgian SE, Cordes EE (2013) Aragonite saturation states at cold-water coral reefs structured by Lophelia pertusa in the northern Gulf of Mexico. Limnology and Oceanography 58: 354-362.

133. Guinotte JM, Orr JC, Cairns S, Freiwald A, Morgan L, et al. (2006) Will human-induced changes in seawater chemistry alter the distribution of deep-sea scleractinian corals? Frontiers in Ecology and the Environment 4: 141-146.

134. Turley CM, Roberts JM, Guinotte JM (2007) Corals in deep-water: will the unseen hand of ocean acidification destroy cold-water ecosystems? Coral Reefs 26: 445-448.

135. Maier C, Hegeman J, Weinbauer MG (2009) Calcification of the cold-water coral *Lophelia pertusa* under ambient and reduced pH. Biogeosciences 6: 1671-1680.

136. Form AU, Riebesell U (2011) Acclimation to ocean acidification during long-term CO_2 exposure in the cold-water coral *Lophelia pertusa*. Global Change Biology 18: 843-853.

137. Hennige S, Wicks LC, Keamenos N, Bakker DCE, Findlay HS, et al. (2014) Short term metabolic and growth responses of the cold-water coral *Lophelia pertusa* to ocean acidification. Deep Sea Research II 99: 27-35.

138. Maier C, Schubert A, Sanchez MMB, Weinbauer MG, Watremez P, et al. (2013) End of the century pCO2 levels do not impact calcification in Mediterranean cold-water corals. Plos One 8.

139. Thresher RE, Tilbrook B, Fallon S, Wilson NC, Adkins J (2011) Effects of chronic low carbonate saturation levels on the distribution, growth and skeletal chemistry of deep-sea corals and other seamount megabenthos. Marine Ecology Progress Series 442: 87-99.

140. Venn A, Tambutté E, Lotto S, D (2009) Imaging intracellular pH in a reef coral and symbiotic anemone. Proceedings of the National Academy of Science 106: 16574-16579.

141. Anagnostou E, Huang KF, You CF, Sikes EL, Sherrell RM (2012) Evaluation of boron isotope ratio as a pH proxy in the deep sea coral Desmophyllum dianthus: Evidence of physiological pH adjustment. Earth and Planetary Science Letters 349: 251-260.

142. McCulloch M, Trotter J, Montagna P, Falter J, Dunbar R, et al. (2012) Resilience of cold-water scleractinian corals to ocean acidification: Boron isotopic systematics of pH and saturation state up-regulation. Geochimica et Cosmochimica Acta 87: 21-34.

143. Wisshak M, Schoenberg CHL, Form A, Freiwald A (2012) Ocean Acidification Accelerates Reef Bioerosion. Plos One 7.

144. Gattuso J-P, Frankignoulle M, Bourge I, Romaine S, Buddemeier RW (1998) Effect of calcium carbonate saturation of seawater on coral calcification. Global and Planetary Change 18: 18p37-46.

145. Kleypas JA, Langdon C (2006) Coral reefs and changing seawater chemistry. In: Phinney JT, Hoegh-Guldberg O, Kleypas JA, Skirving W, Strong A, editors. Coral Reefs and Climate Change: Science and Management. Washington DC: Am. Geophys.

146. Krief S, Hendy EJ, Fine M, Yam R, Meibom A, et al. (2010) Physiological and isotopic responses of scleractinian corals to ocean acidification. Geochimica Et Cosmochimica Acta 74: 4988-5001.

147. Langdon C, Atkinson MJ (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-Oceans 110.

148. Marubini F, Ferrier-Pagès C (2003) Suppression of skeletal growth in scleractinian corals by decreasing ambient carbonate-ion concentration: a cross-family comparison. Proceedings of the Royal Society B: Biological Sciences 270: 179-184.

149. Ohde S, Hossain M (2004) Effect of CaCO3 (aragonite) saturation state of seawater on calcification of *Porites* coral. Geochemical Journal 38: 613-621.

150. Reynaud S, Leclercq N, Romaine- S (2003) Interacting effects of CO_2 partial pressure and temperature on photosynthesis and calcification in a scleractinian coral. Global Change Biology 9: 1660-1668.

151. Wicks LC, Roberts JM (2012) Benthic invertebrates in a high-CO_2 world. Oceanography and Marine Biology: An Annual Review 50: 127-188.

152. Ridd PV, da Silva ET, Stieglitz T (2013) Have coral calcification rates slowed in the last twenty years? Marine Geology 346: 392-399.

153. Ries JB, Cohen AL, McCorkle DC (2010) A nonlinear calcification response to CO_2-induced ocean acidification by the coral *Oculina arbuscula*. Coral Reefs.

154. Kroeker KJ, Kordas RL, Crim RN, Singh GG (2010) Meta-analysis reveals negative yet variable effects of ocean acidification on marine organisms. Ecology Letters 13: 1419-1436.

155. Chan NCS, Connolly SR (2013) Sensitivity of coral calcification to ocean acidification: a meta-analysis. Global Change Biology 19: 282-290.

156. Hoegh-Guldberg O, Mumby P, Hooten A, Steneck R, Greenfield P, et al. (2007) Coral reefs under rapid climate change and ocean acidification. Science 318: 1737.

157. Pandolfi JM, Connolly SRSR, Marshall DJ, Cohen AL (2011) Projecting coral reef futures under global warming and ocean acidification. Science 333: 418-418.

158. Andersson AJ, Gledhill D (2013) Ocean acidification and coral reefs: effects on breakdown, dissolution, and net ecosystem calcification. Ann Rev Mar Sci 5: 321-348.

159. Andersson AJ, Kuffner IB, Mackenzie FT, Jokiel PL, Rodgers KS, et al. (2009) Net Loss of CaCO3 from a subtropical calcifying community due to seawater acidification: mesocosm-scale experimental evidence. Biogeosciences 6: 1811-1823.

160. McCulloch M, Trotter J, Montagna P, Falter J, Dunbar R, et al. (2012) Resilience of cold-water scleractinian corals to ocean acidification: Boron isotopic systematics of pH and saturation state up-regulation. Geochimica et Cosmochimica Acta 87: 21-34.

161. Gazeau F, Parker LM, Comeau S, Gattuso J-P, O'Connor WA, et al. (2013) Impacts of ocean acidification on marine shelled molluscs. Marine Biology 160: 2207-2245.

162. Sanford E, Gaylord B, Hettinger A, Lenz EA, Meyer K, et al. (2014) Ocean acidification increases the vulnerability of native oysters to predation by invasive snails. Proc Biol Sci 281: 20132681.

163. Gazeau F, Quiblier C, Jansen J, Gattuso J-P (2007) Impact of elevated CO_2 on shellfish calcification. Geophysical Research 34: 101029/.

164. Michaelidis B, Ouzounis C, Paleras A, Portner HO (2005) Effects of long-term moderate hypercapnia on acid-base balance and growth rate in marine mussels Mytilus galloprovincialis. Marine Ecology Progress Series 293: 109-118.

165. Thomsen J, Gutowska Ma (2010) Calcifying invertebrates succeed in a naturally CO2 enriched coastal habitat but are threatened by high levels of future acidification. Biogeosciences … 7: 5119-5156.
166. Melzner F, Stange P, Truebenbach K, Thomsen J, Casties I, et al. (2011) Food Supply and Seawater pCO(2) Impact Calcification and Internal Shell Dissolution in the Blue Mussel Mytilus edulis. Plos One 6.
167. Tunnicliffe V, Davies KTA, Butterfield DA, Embley RW, Rose JM, et al. (2009) Survival of mussels in extremely acidic waters on a submarine volcano. Nature Geoscience 2: 344-348.
168. Thomsen J, Melzner F (2010) Moderate seawater acidification does not elicit long-term metabolic depression in the blue mussel Mytilus edulis. Marine Biology.
169. Tomanek L, Zuzow MJ, Ivanina AV, Beniash E, Sokolova IM (2011) Proteomic response to elevated P-CO2 level in eastern oysters, Crassostrea virginica: evidence for oxidative stress. Journal of Experimental Biology 214: 1836-1844.
170. Talmage SC, Gobler CJ (2010) Effects of past, present, and future ocean carbon dioxide concentrations on the growth and survival of larval shellfish. Proceedings of the National Academy of Sciences of the United States of America.
171. Gazeau F, Gattuso J-P, Greaves M, Elderfield H, Peene J, et al. (2011) Effect of Carbonate Chemistry Alteration on the Early Embryonic Development of the Pacific Oyster (Crassostrea gigas). PLoS ONE 6: e23010-e23010.
172. Shirayama Y, Thornton H (2005) Effect of increased atmospheric CO2 on shallow water marine benthos. Journal of Geophysical Research-Oceans 110.
173. Gooding RA, Harley CDG, Tang E (2009) Elevated water temperature and carbon dioxide concentration increase the growth of a keystone echinoderm. Proceedings of the National Academy of Sciences of the United States of America 106: 9316-9321.
174. Appelhans YS, Thomsen J, Pansch C, Melzner F, Wahl M (2012) Sour times: seawater acidification effects on growth, feeding behaviour and acid-base status of Asterias rubens and Carcinus maenas. Marine Ecology Progress Series 459: 85-98.
175. Wood HL, Spicer JI (2008) Ocean acidification may increase calcification rates, but at a cost. Proceedings of the Royal Society of London Series B-Biological Sciences: 1767-1773.
176. Findlay HS, Wood HL, Kendall MA, Spicer JI, Twitchett RJ, et al. (2011) Comparing the impact of high CO2 on calcium carbonate structures in different marine organisms. Marine Biology Research 7: 565-575.
177. Stumpp M, Trübenbach K, Brennecke D, Hu MY, Melzner F (2012) Resource allocation and extracellular acid-base status in the sea urchin Strongylocentrotus droebachiensis in response to CO(2) induced seawater acidification. Aquatic toxicology (Amsterdam, Netherlands) 110-111C: 194-207.
178. Sunday JM, Crim RN, Harley CDG, Hart MW (2011) Quantifying Rates of Evolutionary Adaptation in Response to Ocean Acidification. PLoS ONE 6.
179. Dupont S, Dorey N, Stumpp M, Melzner F, Thorndyke M (2013) Long-term and trans-life-cycle effects of exposure to ocean acidification in the green sea urchin Strongylocentrotus droebachiensis. Marine Biology 160: 1835-1843.
180. Porzio L, Buia MC, Hall-Spencer JM (2011) Effects of ocean acidification on macroalgal communities. Journal of Experimental Marine Biology and Ecology 400: 278-287.
181. Connell SD, Russell BD (2010) The direct effects of increasing CO_2 and temperature on non-calcifying organisms: increasing the potential for phase shifts in kelp forests. Proceedings of the Royal Society B: Biological Sciences 277: 1409-1415.
182. Roleda MY, Morris JN, McGraw CM, Hurd CL (2012) Ocean acidification and seaweed reproduction: increased CO2 ameliorates the negative effect of lowered pH on meiospore germination in the giant kelp Macrocystis pyrifera (Laminariales, Phaeophyceae). Global Change Biology 18: 854-864.
183. Johnson VR, Russell BD, Fabricius KE, Brownlee C, Hall-Spencer JM (2012) Temperate and tropical brown macroalgae thrive, despite decalcification, along natural CO2 gradients. Global Change Biology 18: 2792-2803.
184. Gao K, Aruga Y, Asada K, Ishihara T, Akano T, et al. (1991) Enhanced Growth of the Red Alga Porphyra-Yezoensis Ueda in High Co2 Concentrations. Journal of Applied Phycology 3: 355-362.
185. Gao K, Aruga Y, Asada K, Ishihara T, Akano T, et al. (1993) Calcification in the Articulated Coralline Alga Corallina-Pilulifera, with Special Reference to the Effect of Elevated Co2 Concentration. Marine Biology 117: 129-132.
186. Gao KS, Helbling EW, Hader DP, Hutchins DA (2012) Responses of marine primary producers to interactions between ocean acidification, solar radiation, and warming. Marine Ecology Progress Series 470: 167-189.
187. Bauer JE, Cai WJ, Raymond PA, Bianchi TS, Hopkinson CS, et al. (2013) The changing carbon cycle of the coastal ocean. Nature 504: 61-70.
188. Unsworth RKF, Collier CJ, Henderson GM, McKenzie LJ (2012) Tropical seagrass meadows modify seawater carbon chemistry: implications for coral reefs impacted by ocean acidification. Environmental Research Letters 7.
189. Hendriks IE, Olsen YS, Ramajo L, Basso L, Steckbauer A, et al. (2013) Photosynthetic activity buffers ocean acidification in seagrass meadows. Biogeosciences Discussions 10: 12313-12346.
190. Kuffner IB, Andersson AJ, Jokiel PL, Rodgers KuS, Mackenzie FT (2008) Decreased abundance of crustose coralline algae due to ocean acidification. Nature Geoscience 1: 114-117.
191. Martin S, Gattuso J-P (2009) Response of Mediterranean coralline algae to ocean acidification and elevated temperature. Global Change Biology 15: 2089-2100.
192. Arnold T, Mealey C, Leahey H, Miller AW, Hall-Spencer JM, et al. (2012) Ocean Acidification and the Loss of Phenolic Substances in Marine Plants. Plos One 7.
193. Armstrong RA, Lee C, Hedges JI, Honjo S, Wakeham SG (2002) A new, mechanistic model for organic carbon fluxes in the ocean based on the quantitative association of POC with ballast minerals. Deep-Sea Research Part Ii-Topical Studies in Oceanography 49: 219-236.
194. Klaas C, Archer DE (2002) Association of sinking organic matter with various types of mineral ballast in the deep sea: Implications for the rain ratio. Global Biogeochem Cycles 16: 1116.
195. Riebesell U, Tortell PD (2011) Effects of ocean acidification on pelagic organisms and ecosystems. In: Gattuso JP, Hansson L, editors. Ocean Acidification. Oxford: Oxford University Press.
196. Wu Y, Gao K, Riebesell U (2010) CO2-induced seawater acidification affects physiological performance of the marine diatom Phaeodactylum tricornutum. Biogeosciences 7: 2915-2923.
197. Rost B, Richter KU, Riebesell U, Hansen PJ (2006) Inorganic carbon acquisition in red tide dinoflagellates. Plant Cell and Environment 29: 810-822.
198. Kranz SA, Sueltemeyer D, Richter K-U, Rost B (2009) Carbon acquisition by Trichodesmium: The effect of pCO(2) and diurnal changes. Limnology and Oceanography 54: 548-559.

199. Wu YP, Gao KS (2010) Combined effects of solar UV radiation and CO2-induced seawater acidification on photosynthetic carbon fixation of phytoplankton assemblages in the South China Sea. Chinese Science Bulletin 55: 3680-3686.
200. Yang GY, Gao KS (2012) Physiological responses of the marine diatom Thalassiosira pseudonana to increased pCO(2) and seawater acidity. Marine Environmental Research 79: 142-151.
201. Falkowski PG, Katz ME, Knoll AH, Quigg A, Raven JA, et al. (2004) The evolution of modern eukaryotic phytoplankton. Science 305: 354-360.
202. Rost B, Zondervan I, Wolf-Gladrow D (2008) Sensitivity of phytoplankton to future changes in ocean carbonate chemistry: current knowledge, contradictions and research directions. Marine Ecology Progress Series 373: 227-237.
203. Gao KS, Xu JT, Gao G, Li YH, Hutchins DA, et al. (2012) Rising CO2 and increased light exposure synergistically reduce marine primary productivity. Nature Climate Change 2: 519-523.
204. Lundholm N, Hansen PJ, Kotaki Y (2004) Effect of pH on growth and domoic acid production by potentially toxic diatoms of the genera Pseudo-nitzschia and Nitzschia. Marine Ecology Progress Series 273: 1-15.
205. Trimborn S, Lundholm N, Thoms S, Richter KU, Krock B, et al. (2008) Inorganic carbon acquisition in potentially toxic and non-toxic diatoms: the effect of pH-induced changes in seawater carbonate chemistry. Physiologia Plantarum 133: 92-105.
206. Fu FX, Tatters AO, Hutchins DA (2012) Global change and the future of harmful algal blooms in the ocean. Marine Ecology Progress Series 470: 207-233.
207. Riebesell U (2004) Effects of CO 2 enrichment on marine phytoplankton. Journal of Oceanography 60: 719-729.
208. Riebesell U, Zondervan I, Rost B, Tortell PD, Zeebe RE, et al. (2000) Reduced calcification of marine plankton in response to increased atmospheric CO2. Nature 407: 364-367.
209. Zondervan I, Rost BÈ, Riebesell U (2002) Effect of CO2 concentration on the PIC/POC ratio in the coccolithophore Emiliania huxleyi grown under light-limiting conditions and different daylengths. Journal of Experimental Marine Biology and Ecology 272: 55-70.
210. Engel A, Zondervan I, Aerts K, Beaufort L, Benthien A, et al. (2005) Testing the direct effect of CO2 concentration on a bloom of the coccolithophorid Emiliania huxleyi in mesocosm experiments. Limnology and Oceanography 50: 493-507.
211. Gao KS, Ruan ZX, Villafane VE, Gattuso JP, Helbling EW (2009) Ocean acidification exacerbates the effect of UV radiation on the calcifying phytoplankter Emiliania huxleyi. Limnology and Oceanography 54: 1855-1862.
212. Merico A, Tyrrell T, Cokacar T (2006) Is there any relationship between phytoplankton seasonal dynamics and the carbonate system? Journal of Marine Systems 59: 120-142.
213. Tyrrell T, Schneider B, Charalampopoulou A, Riebesell U (2008) Coccolithophores and calcite saturation state in the Baltic and Black Seas. Biogeosciences 5: 485-494.
214. Cubillos JC, Wright SW, Nash G, de Salas MF, Griffiths B, et al. (2007) Calcification morphotypes of the coccolithophorid Emiliania huxleyi in the Southern Ocean: changes in 2001 to 2006 compared to historical data. Marine Ecology Progress Series 348: 47-54.
215. Beaufort L, Probert I, de Garidel-Thoron T, Bendif EM, Ruiz-Pino D, et al. (2011) Sensitivity of coccolithophores to carbonate chemistry and ocean acidification. Nature 476: 80-83.
216. Langer G, Geisen M, Baumann K-H, Klaes J, Riebesell U, et al. (2006) Species-specific responses of calcifying algae to changing seawater carbonate chemistry. Geochemistry Geophysics Geosystems 7.
217. Iglesias-Rodriguez MDD, Halloran PRPR, Rickaby REM, Hall IR, Colmenero-Hidalgo E, et al. (2008) Phytoplankton calcification in a high-CO2 world. Science (New York, NY) 320: 336-340.
218. Lohbeck KT, Riebesell U, Reusch TBH (2012) Adaptive evolution of a key phytoplankton species to ocean acidification. Nature Geoscience 5: 346-351.
219. Jin P, Gao KS, Beardall J (2013) Evolutionary Responses of a Coccolithophorid Gephyrocapsa Oceanica to Ocean Acidification. Evolution 67: 1869-1878.
220. Grelaud M, Schimmelmann A, Beaufort L (2009) Coccolithophore response to climate and surface hydrography in Santa Barbara Basin, California, AD 1917-2004. Biogeosciences 6: 2025-2039.
221. Aberle N, Schulz KG, Stuhr A, Malzahn AM, Ludwig A, et al. (2013) High tolerance of microzooplankton to ocean acidification in an Arctic coastal plankton community. Biogeosciences 10: 1471-1481.
222. Czerny J, Schulz KG, Boxhammer T, Bellerby RGJ, Buedenbender J, et al. (2013) Implications of elevated CO2 on pelagic carbon fluxes in an Arctic mesocosm study - an elemental mass balance approach. Biogeosciences 10: 3109-3125.
223. Webster NS, Negri AP, Flores F, Humphrey C, Soo R, et al. (2013) Near-future ocean acidification causes differences in microbial associations within diverse coral reef taxa. Environmental Microbiology Reports 5: 243-251.
224. Laverock B, Kitidis V, Tait K, Gilbert JA, Osborn AM, et al. (2013) Bioturbation determines the response of benthic ammonia-oxidizing microorganisms to ocean acidification. Philos Trans R Soc Lond B Biol Sci 368: 20120441.
225. Lalii CM, Gilmer RW (1989) Pelagic snails: The biology of holoplanktonic gastropod mollusks. Stanford, CA: Stanford University Press.
226. Hunt BPV, Pakhomov EA, Hosie GW, Siegel V, Ward P, et al. (2008) Pteropods in Southern Ocean ecosystems. Progress in Oceanography 78: 193-221.
227. Teniswood CMH, Roberts D, Howard WR, Bradby JE (2013) A quantitative assessment of the mechanical strength of the polar pteropod Limacina helicina antarctica shell. Ices Journal of Marine Science 70: 1499-1505.
228. Feely RA, Sabine CL, Lee K, Berelson WM, Kleypas JA, et al. (2004) Impact of anthropogenic CO_2 on the $CaCO_3$ system in the oceans. Science 305: 362.
229. Bednarsek N, Tarling GA, Bakker DCE, Fielding S, Jones EM, et al. (2012) Extensive dissolution of live pteropods in the Southern Ocean. Nature Geoscience 5: 881-885.
230. Comeau S, Gorsky G, Jeffree R, Teyssié J-L, Gattuso J-P (2009) Impact of ocean acidification on a key Arctic pelagic mollusc (Limacina helicina). Biogeosciences 6: 1877-1882.
231. Comeau S, Gorsky G, Alliouane S, Gattuso J-P (2010) Larvae of the pteropod *Cavolinia inflexa* exposed to aragonite undersaturation are viable but shell-less. Marine Biology 157: 2341-2345.
232. Comeau S, Jeffree R, Teyssié J-L, Gattuso J-P (2010) Response of the Arctic pteropod Limacina helicina to projected future environmental conditions. PloS one 5: e11362.
233. Lischka S, Buedenbender J, Boxhammer T, Riebesell U (2011) Impact of ocean acidification and elevated temperatures on early juveniles of the polar shelled pteropod Limacina helicina: mortality, shell degradation, and shell growth. Biogeosciences 8: 919-932.
234. Lischka S, Riebesell U (2012) Synergistic effects of ocean acidification and warming on overwintering pteropods in the Arctic. Global Change Biology 18: 3517-3528.

235. Mackas DL, Galbraith MD (2012) Pteropod time-series from the NE Pacific. Ices Journal of Marine Science 69: 448-459.
236. Comeau S, Gattuso J-P, Nisumaa A-M, Orr J (2012) Impact of aragonite saturation state changes on migratory pteropods. Proceedings of the Royal Society B-Biological Sciences 279: 732-738.
237. Comeau S, Jeffree R, Teyssie JL, Gattuso JP (2010) Response of the Arctic Pteropod Limacina helicina to Projected Future Environmental Conditions. PLoS ONE 5.
238. Schiebel R (2002) Planktic foraminiferal sedimentation and the marine calcite budget. Global Biogeochemical Cycles 16.
239. Bijma J, Honisch B, Zeebe RE (2002) Impact of the ocean carbonate chemistry on living foraminiferal shell weight: Comment on "Carbonate ion concentration in glacial-age deep waters of the Caribbean Sea" by W. S. Broecker and E. Clark. Geochemistry Geophysics Geosystems 3.
240. Bjima J., Spero HJ, Lea DW (1999) Reassessing foraminiferal stable isotope geochemistry: Impact of theoceanic carbonate system (experimental results). In: Fisher G., G. W, editors. Use of Proxies in Paleoceanography: Examples from the South Atlantic. New York: Springer-Verlag.
241. Russell AD, Honisch B, Spero HJ, Lea DW (2004) Effects of seawater carbonate ion concentration and temperature on shell U, Mg, and Sr in cultured planktonic foraminifera. Geochimica Et Cosmochimica Acta 68: 4347-4361.
242. Spero HJ, Bijma J, Lea DW, Bemis BE (1997) Effect of seawater carbonate concentration on foraminiferal carbon and oxygen isotopes. NATURE-LONDON- 390: 497-499.
243. Lombard F, da Rocha RE, Bijma J, Gattuso JP (2010) Effect of carbonate ion concentration and irradiance on calcification in planktonic foraminifera. Biogeosciences 7: 247-255.
244. Barker S, Elderfield H (2002) Foraminiferal calcification response to glacial-interglacial changes in atmospheric CO2. Science 297: 833-836.
245. de Moel H, Ganssen GM, Peeters FJC, Jung SJA, Kroon D, et al. (2009) Planktic foraminiferal shell thinning in the Arabian Sea due to anthropogenic ocean acidification? Biogeosciences 6: 1917-1925.
246. Moy AD, Howard WR, Bray SG, Trull TW (2009) Reduced calcification in modern Southern Ocean planktonic foraminifera. Nature Geoscience 2: 276-280.
247. Fujita K, Hikami M, Suzuki A, Kuroyanagi A, Sakai K, et al. (2011) Effects of ocean acidification on calcification of symbiont-bearing reef foraminifers. Biogeosciences 8: 2089-2098.
248. Davis CV, Badger MPS, Bown PR, Schmidt DN (2013) Calcification responses to climate change in the Pliocene. Biogeosciences Discussions 10: 6840-6860.
249. H.B. B (1884) Report on the Foraminifera dredged by HMS Challenger, during the years 1873-1876, Reports of the Scientific Results of the Voyage of HMS Challenger. Zoology 9: 814.
250. Longhurst AR (1985) The structure and evolution of plankton communities. Progress in Oceanography 15: 1-35.
251. Runge JA (1988) Should we expect a relationship between primary production and fisheries - the role of copepod dynamics as a filter of trophic variability. Hydrobiologia 167: 61-71.
252. Kurihara H, Shirayama Y (2004) Effects of increased atmospheric CO~ 2 on sea urchin early development. Marine Ecology Progress Series 274: 161-169.
253. Mayor D, Matthews C, Cook K, Zuur A, Hay S (2007) CO2-induced acidification affects hatching success in Calanus finmarchicus. Marine Ecology Progress Series 350: 91-97.
254. Weydmann A, Soreide JE, Kwasniewski S, Widdicombe S (2012) Influence of CO2-induced acidification on the reproduction of a key Arctic copepod Calanus glacialis. Journal of Experimental Marine Biology and Ecology 428: 39-42.
255. McConville K, Halsband C, Fileman ES, Somerfield PJ, Findlay HS, et al. (2013) Effects of elevated CO2 on the reproduction of two calanoid copepods. Marine Pollution Bulletin 73: 428-434.
256. Watanabe Y, Yamaguchi A, Ishidai H, Harimoto T, Suzuki S, et al. (2006) Lethality of increasing CO2 levels on deep-sea copepods in the western North Pacific. Journal of Oceanography 62: 185-196.
257. Niehoff B, Schmithuesen T, Knueppel N, Daase M, Czerny J, et al. (2013) Mesozooplankton community development at elevated CO2 concentrations: results from a mesocosm experiment in an Arctic fjord. Biogeosciences 10: 1391-1406.
258. de Kluijver A, Soetaert K, Czerny J, Schulz KG, Boxhammer T, et al. (2013) A C-13 labelling study on carbon fluxes in Arctic plankton communities under elevated CO2 levels. Biogeosciences 10: 1425-1440.
259. Li W, Gao KS (2012) A marine secondary producer respires and feeds more in a high CO2 ocean. Marine Pollution Bulletin 64: 699-703.
260. Rossoll D, Bermudez R, Hauss H, Schulz KG, Riebesell U, et al. (2012) Ocean Acidification-Induced Food Quality Deterioration Constrains Trophic Transfer. Plos One 7.
261. Claiborne JB, Edwards SL, Morrison-Shetlar AI (2002) Acid-base regulation in fishes: Cellular and molecular mechanisms. Journal of Experimental Zoology 293: 302-319.
262. Brauner CJ, Baker DW (2009) Patterns of Acid-Base Regulation During Exposure to Hypercarbia in Fishes; Glass ML, Wood SC, editors. 43-63 p.
263. Ishimatsu A, Hayashi M, Kikkawa T (2008) Fishes in high-CO2, acidified oceans. Marine Ecology Progress Series 373: 295-302.
264. Pörtner HO, Farrell AP (2008) Physiology And Climate Change. Science: 690-692.
265. Munday PL, Crawley NE, Nilsson GE (2009) Interacting effects of elevated temperature and ocean acidification on the aerobic performance of coral reef fishes. Marine Ecology Progress Series 388: 235-242.
266. Melzner F, Goebel S, Langenbuch M, Gutowska MA, Poertner H-O, et al. (2009) Swimming performance in Atlantic Cod (Gadus morhua) following long-term (4-12 months) acclimation to elevated seawater P-CO2. Aquatic Toxicology 92: 30-37.
267. McKenzie DJ, Piccolella M, Dalla Valle AZ, Taylor EW, Bolis CL, et al. (2003) Tolerance of chronic hypercapnia by the European eel Anguilla anguilla. Journal of Experimental Biology 206: 1717-1726.
268. Tresguerres M, Parks SK, Salazar E, Levin LR, Goss GG, et al. (2010) Bicarbonate-sensing soluble adenylyl cyclase is an essential sensor for acid/base homeostasis. Proceedings of the National Academy of Sciences of the United States of America 107: 442-447.
269. Munday PL, Donelson JM, Dixson DL, Endo GGK (2009) Effects of ocean acidification on the early life history of a tropical marine fish. Proceedings Biological sciences / The Royal Society 276: 3275-3283.
270. Munday PL, Gagliano M, Donelson JM, Dixson DL, Thorrold SR (2011) Ocean acidification does not affect the early life history development of a tropical marine fish. Marine Ecology Progress Series 423: 211-221.
271. Bignami S, Sponaugle S, Cowen RK (2013) Response to ocean acidification in larvae of a large tropical marine fish, Rachycentron canadum. Global Change Biology 19: 996-1006.

272. Hurst TP, Fernandez ER, Mathis JT, Miller JA, Stinson CM, et al. (2012) Resiliency of juvenile walleye pollock to projected levels of ocean acidification. Aquatic Biology 17: 247-259.
273. Baumann H, Talmage SC, Gobler CJ (2012) Reduced early life growth and survival in a fish in direct response to increased carbon dioxide. Nature Climate Change 2: 38-41.
274. Frommel AY, Maneja R, Lowe D, Malzahn AM, Geffen AJ, et al. (2012) Severe tissue damage in Atlantic cod larvae under increasing ocean acidification. Nature Climate Change 2: 42-46.
275. Frommel AY, Schubert A, Piatkowski U, Clemmesen C (2013) Egg and early larval stages of Baltic cod, Gadus morhua, are robust to high levels of ocean acidification. Marine Biology 160: 1825-1834.
276. Miller GM, Watson S-A, Donelson JM, McCormick MI, Munday PL (2012) Parental environment mediates impacts of increased carbon dioxide on a coral reef fish. Nature Climate Change 2: 858-861.
277. Miller GM, Watson SA, McCormick MI, Munday PL (2013) Increased CO2 stimulates reproduction in a coral reef fish. Global Change Biology 19: 3037-3045.
278. Inaba K, Dreanno C, Cosson J (2003) Control of flatfish sperm motility by CO2 and carbonic anhydrase. Cell Motility and the Cytoskeleton 55: 174-187.
279. Frommel AY, Stiebens V, Clemmesen C, Havenhand J (2010) Effect of ocean acidification on marine fish sperm (Baltic cod: Gadus morhua). Biogeosciences 7: 3915-3919.
280. Franke A, Clemmesen C (2011) Effect of ocean acidification on early life stages of Atlantic herring (Clupea harengus L.). Biogeosciences 8: 3697-3707.
281. Checkley DM, Dickson AG, Takahashi M, Radich JA, Eisenkolb N, et al. (2009) Elevated CO2 enhances otolith growth in young fish. Science (New York, NY) 324: 1683.
282. Munday PL, Hernaman V, Dixson DL, Thorrold SR (2011) Effect of ocean acidification on otolith development in larvae of a tropical marine fish. Biogeosciences 8: 1631-1641.
283. Maneja RH, Frommel AY, Geffen AJ, Folkvord A, Piatkowski U, et al. (2013) Effects of ocean acidification on the calcification of otoliths of larval Atlantic cod Gadus morhua. Marine Ecology Progress Series 477: 251-258.
284. Bignami S, Enochs IC, Manzello DP, Sponaugle S, Cowen RK (2013) Ocean acidification alters the otoliths of a pantropical fish species with implications for sensory function. Proceedings of the National Academy of Sciences of the United States of America 110: 7366-7370.
285. Portner HO, Zielinski S (1998) Environmental constraints and the physiology of performance in squid. South African Journal of Marine Science-Suid-Afrikaanse Tydskrif Vir Seewetenskap 20: 207-221.
286. Portner HO (1994) Coordination of metabolism, acid-base regulation and haemocyanin function in cephalopods; Portner HO, O'Dor RK, Macmillan DL, editors. 131-148 p.
287. Pörtner HO, Langenbuch M, Reipschlager A (2004) Biological impact of elevated ocean CO 2 concentrations: lessons from animal physiology and earth history. Journal of Oceanography 60: 705-718.
288. Rosa RA, Seibel BA (2008) Synergistic effects of climate-related variables suggest future physiological impairment in a top oceanic predator. Proceedings of the National Academy of Sciences 105: 20776.
289. Kaplan MB, Mooney TA, McCorkle DC, Cohen AL (2013) Adverse Effects of Ocean Acidification on Early Development of Squid (Doryteuthis pealeii). Plos One 8.
290. Dorey N, Melzner F, Martin S, Oberhaensli F, Teyssie J-L, et al. (2013) Ocean acidification and temperature rise: effects on calcification during early development of the cuttlefish Sepia officinalis. Marine Biology 160: 2007-2022.
291. Rosa R, Truebenbach K, Repolho T, Pimentel M, Faleiro F, et al. (2013) Lower hypoxia thresholds of cuttlefish early life stages living in a warm acidified ocean. Proceedings of the Royal Society B-Biological Sciences 280.
292. Cooley SR, Kite-Powell HL, Doney SC (2009) Ocean Acidification's Potential to Alter Global Marine Ecosystem Services. Oceanography 22: 172-181.
293. Busch DS, Harvey CJ, McElhany P (2013) Potential impacts of ocean acidification on the Puget Sound food web. Ices Journal of Marine Science 70: 823-833.
294. Fisher B, Turner RK, Morling P (2009) Defining and classifying ecosystem services for decision making. Ecological Economics 68: 643-653.
295. Fisher B, Turner K, Zylstra M, Brouwer R, de Groot R, et al. (2008) Ecosystem services and economic theory: integration for policy-relevant research. Ecological Applications 18: 2050-2067.
296. Turner RK, Paavola J, Cooper P, Farber S, Jessamy V, et al. (2003) Valuing nature: lessons learned and future research directions. Ecological Economics 46: 493-510.
297. MA (Millennium Ecosystem Assessment). Ecosystems and Human Well-being: A Framework for Assessment. 2003 Washington DC
298. Levitan O, Rosenberg G, Setlik I, Setlikova E, Grigel J, et al. (2007) Elevated CO_2 enhances nitrogen fixation and growth in the marine cyanobacterium *Trichodesmium*. Global Change Biology 13: 531-538.
299. Kerr Ra (2010) Ocean acidification unprecedented, unsettling. Science 328: 1500-1501.
300. Barton A, Hales B, Waldbusser GG, Langdon C, Feely RA (2012) The Pacific oyster, Crassostrea gigas, shows negative correlation to naturally elevated carbon dioxide levels: Implications for near-term ocean acidification effects. Limnology and Oceanography 57: 698-710.
301. Cooley SR, Lucey N, Kite-Powell H, Doney SC (2012) Nutrition and income from molluscs today imply vulnerability to ocean acidification tomorrow. Fish and Fisheries 13: 182-215.
302. Le Quesne WJF, Pinnegar JK (2011) The potential impacts of ocean acidification: scaling from physiology to fisheries*. Fish and Fisheries 13: no-no.
303. Bos AR, Bouma TJ, de Kort GLJ, van Katwijk MM (2007) Ecosystem engineering by annual intertidal seagrass beds: Sediment accretion and modification. Estuarine Coastal and Shelf Science 74: 344-348.
304. Feagin RA, Lozada-Bernard SM, Ravens TM, Moeller I, Yeager KM, et al. (2009) Does vegetation prevent wave erosion of salt marsh edges? Proceedings of the National Academy of Sciences of the United States of America 106: 10109-10113.
305. Pacific Coast Shellfish Growers Association http://www.pcsga.org/pub/farming/production_stats.pdf
306. Cheung WWL, Dunne J, Sarmiento JL, Pauly D (2011) Integrating ecophysiology and plankton dynamics into projected maximum fisheries catch potential under climate change in the Northeast Atlantic. Ices Journal of Marine Science 68: 1008-1018.
307. Sumaila UR, Cheung WWL, Lam VWY, Pauly D, Herrick S (2011) Climate change impacts on the biophysics and economics of world fisheries. Nature Climate Change 1: 449-456.

308. Brander L.M., Narita D, Rehdanz K, Tol RSJ (In press) The economic impact of ocean acidification. In: Paulo A.L.D., Nunes PALD, P. K, T. D, editors. Economics of biodiversity and ecosystem services: Edward Elgar.
309. Armstrong C., Holen S., Navrud S., (2012) The Economics of Ocean Acidification – a scoping study. 2012 Norway: FRAM Centre
310. Brander LM, Rehdanz K, Tol RSJ, P. vB (2012) The economic impact of ocean acidification on coral reefs. Climate Change Economics 3.
311. Cooley SR, Doney SC (2009) Anticipating ocean acidification's economic consequences for commercial fisheries. Environmental Research Letters 4.
312. Finnoff D (2010) Modeling economic impacts of climate change and ocean acidification to fisheries. http://yosemite.epa.gov/ee/epa/eerm.nsf/vwAN/EE-0566-115.pdf/$file/EE-0566-115.pdf
313. Harrould-Kolieb ER, Hirshfield M, Brosius A (2009) Major Emitters Among Hardest Hit by OA: An Analysis of the Impacts of Acidification on the Countries of the World. Washington DC
314. Hilmi N, Allemand D, Dupont S, Safa A, Haraldsson G, et al. (2013) Towards improved socio-economic assessments of ocean acidification's impacts. Marine Biology 160: 1773-1787.
315. Kite-Powell H (2009) A Global Perspective on the Economics of Ocean Acidification. Current 25: 25-29.
316. Moore C (2011) Welfare impacts of ocean acidification: An integrated assessment model of the US mollusk fishery. 2011
317. Narita D, Rehdanz K, Tol RSJ (2012) Economic costs of ocean acidification: a look into the impacts on global shellfish production. Climatic Change 113: 1049-1063.
318. Rodrigues LC, van den Bergh JCJM, Ghermandi A (2013) Socio-economic impacts of ocean acidification in the Mediterranean Sea. Marine Policy 38: 447-456.
319. Noone KJ, Sumaila UR, Diaz RJ (2013) Managing ocean environments in a changing climate: sustainability and economic perspectives: Elsevier.
320. Gehlen M, Gruber N, Gangsto R, Bopp L, Oschlies A (2011) Biogeochemical consequences of ocean acidification and feedbacks to the earth system. In: Gattuso JP, Hansson L, editors. Ocean Acidification. Oxford: Oxford University Press. pp. 230-248.
321. Brewer PG, Peltzer ET (2009) Limits to marine life. Science 324: 347-348.
322. Schneider B, Bopp L, Gehlen M, Segschneider J, Froelicher TL, et al. (2008) Climate-induced interannual variability of marine primary and export production in three global coupled climate carbon cycle models. Biogeosciences 5: 597-614.
323. Riebesell U, Schulz K, Bellerby R, Botros M, P (2007) Enhanced biological carbon consumption in a high CO2 ocean. Nature 450.
324. Bellerby RGJ, Schulz KG, Riebesell U, Neill C, Nondal G, et al. (2008) Marine ecosystem community carbon and nutrient uptake stoichiometry under varying ocean acidification during the PeECE III experiment. Biogeosciences 5: 1517-1527.
325. Oschlies A, Schulz KG, Riebesell U, Schmittner A (2008) Simulated 21st century's increase in oceanic suboxia by CO2-enhanced biotic carbon export. Global Biogeochemical Cycles 22.
326. Hutchins DA, Mulholland MR, Fu F (2009) Nutrient Cycles and Marine Microbes in a CO2-Enriched Ocean. Oceanography 22: 128-145.
327. Hutchins DA, Fu FX, Webb EA, Walworth N, Tagliabue A (2013) Taxon-specific response of marine nitrogen fixers to elevated carbon dioxide concentrations. Nature Geoscience 6: 790-795.
328. Fu F-X, Mulholland MR, Garcia NS, Beck A, Bernhardt PW, et al. (2008) Interactions between changing pCO(2), N-2 fixation, and Fe limitation in the marine unicellular cyanobacterium Crocosphaera. Limnology and Oceanography 53: 2472-2484.
329. Law CS, Breitbarth E, Hoffmann LJ, McGraw CM, Langlois RJ, et al. (2012) No stimulation of nitrogen fixation by non-filamentous diazotrophs under elevated CO2 in the South Pacific. Global Change Biology 18: 3004-3014.
330. Shi DL, Kranz SA, Kim JM, Morel FMM (2012) Ocean acidification slows nitrogen fixation and growth in the dominant diazotroph *Trichodesmium* under low-iron conditions. Proceedings of the National Academy of Sciences of the United States of America 109: E3094-E3100.
331. Shi D, Xu Y, Hopkinson BM, Morel FMM (2010) Effect of Ocean Acidification on Iron Availability to Marine Phytoplankton. Science 327: 676-679.
332. Trull TW, Bray SG, Manganini SJ, Honjo S, Francois R (2001) Moored sediment trap measurements of carbon export in the Subantarctic and Polar Frontal Zones of the Southern Ocean, south of Australia. Journal of Geophysical Research-Oceans 106: 31489-31509.
333. Piontek J, Lunau M, Haendel N, Borchard C, Wurst M, et al. (2010) Acidification increases microbial polysaccharide degradation in the ocean. Biogeosciences 7: 1615-1624.
334. Maas EW, Law CS, Hall JA, Pickmere S, Currie KI, et al. (2013) Effect of ocean acidification on bacterial abundance, activity and diversity in the Ross Sea, Antarctica. Aquatic Microbial Ecology 70: 1-15.
335. Hopkins F, Nightingale P, Liss P (2011) Effects of ocean acidification on the marine source of atmospherically active trace gases. In: Gattuso JP, Hansson L, editors. Ocean Acidification. Oxford: Oxford University Press.
336. Six KD, Kloster S, Ilyina T, Archer SD, Zhang K, et al. (2013) Global warming amplified by reduced sulphur fluxes as a result of ocean acidification. Nature Climate Change 3: 975-978.
337. Matear R, Chamberlain MA, Lenton A (Submitted) Biogeochemical consequences of ocean acidification and feedbacks to the Earth system. Biogeochemistry Discussions.
338. Cocco V, Joos F, Steinacher M, Froelicher TL, Bopp L, et al. (2013) Oxygen and indicators of stress for marine life in multi-model global warming projections. Biogeosciences 10: 1849-1868.
339. Bopp L, Resplandy L, Orr JC, Doney SC, Dunne JP, et al. (2013) Multiple stressors of ocean ecosystems in the 21st century: projections with CMIP5 models. Biogeosciences 10: 6225-6245.
340. Tagliabue A, Bopp L, Gehlen M (2011) The response of marine carbon and nutrient cycles to ocean acidification: Large uncertainties related to phytoplankton physiological assumptions. Global Biogeochemical Cycles 25.
341. Matear RJ, Hirst AC, McNeil BI (2000) Changes in dissolved oxygen in the Southern Ocean with climate change. Geochemistry Geophysics Geosystems 1.
342. Bopp L, Le Quere C, Heimann M, Manning AC, Monfray P (2002) Climate-induced oceanic oxygen fluxes: Implications for the contemporary carbon budget. Global Biogeochemical Cycles 16.
343. Matear RJ, Wang Y-P, Lenton A (2010) Land and ocean nutrient and carbon cycle interactions. Current Opinion in Environmental Sustainability 2: 258-263.
344. Gruber N, Galloway JN (2008) An Earth-system perspective of the global nitrogen cycle. Nature 451: 293-296.
345. Glessmer MS, Eden C, Oschlies A (2009) Contribution of oxygen minimum zone waters to the coastal upwelling off Mauritania. Progress in Oceanography 83: 143-150.

346. Schmittner A, Oschlies A, Matthews HD, Galbraith ED (2008) Future changes in climate, ocean circulation, ecosystems, and biogeochemical cycling simulated for a business-as-usual CO2 emission scenario until year 4000 AD. Global Biogeochemical Cycles 22.
347. Biastoch A, Treude T, Rüpke LH, Riebesell U, Roth C, et al. (2011) Rising Arctic Ocean temperatures cause gas hydrate destabilization and ocean acidification. Geophysical Research Letters 38: n/a-n/a.
348. Gabric A, Murray N, Stone L, Kohl M (1993) Modeling the production of dimethylsulfide during a phytoplankton bloom. Journal of Geophysical Research-Oceans 98: 22805-22816.
349. Arnold HE, Kerrison P, Steinke M (2013) Interacting effects of ocean acidification and warming on growth and DMS-production in the haptophyte coccolithophore Emiliania huxleyi. Global Change Biology 19: 1007-1016.
350. Cameron-Smith P, Elliott S, Maltrud M, Erickson D, Wingenter O (2011) Changes in dimethyl sulfide oceanic distribution due to climate change. Geophysical Research Letters 38.
351. Kloster S, Six KD, Feichter J, Maier-Reimer E, Roeckner E, et al. (2007) Response of dimethylsulfide (DMS) in the ocean and atmosphere to global warming. Journal of Geophysical Research-Biogeosciences 112.
352. Gabric AJ, Qu B, Matrai P, Hirst AC (2005) The simulated response of dimethylsulfide production in the Arctic Ocean to global warming. Tellus Series B-Chemical and Physical Meteorology 57: 391-403.
353. Woodhouse MT, Mann GW, Carslaw KS, Boucher O (2013) Sensitivity of cloud condensation nuclei to regional changes in dimethyl-sulphide emissions. Atmospheric Chemistry and Physics 13: 2723-2733.

6 FUTURE CONSIDERATIONS

6.1 Technical challenges: from individuals to ecosystems

Key Messages: Chapter 6

1. A true multidisciplinary approach involving technological challenges is needed

2. Research should be oriented toward a quantitative understanding at all levels from chemistry to socio-economics

3. Research should be solution–oriented, covering the scale from local to global, and should prioritize the ecosystems and societies most at risk

4. A high density of measurements in space and time are required to identify variability and anthropogenically induced ocean acidification

5. Autonomous systems will remove the need of operators and encourage the development of low cost, low power, long-term measurement techniques

A large body of scientific information about ocean acidification was rapidly generated during the past few years, contributing to increased political awareness. The field evolved from an exploratory phase leading to several key proof-of-concepts, toward more hypothesis-driven research [1,2]. Key factors modulating responses of species, ecosystems and their services were identified and include environmental variability [3], ecological interactions[4], species potential for acclimation and adaptation [5] and multiple drivers. Ideally, an experiment assessing the impact of ocean acidification on a given species/ecosystem should include the whole ecosystem, natural variability [6] and realistic rates of change for all environmental drivers (CO_2, temperature, salinity, food concentrations, light availability), and be long term (i.e. several years) to allow multiple generations of each species in the ecosystem. Multiple endpoints from physiological response to biodiversity and socio-economic impacts should also be considered (Table 6.1). Such experiments should be replicated several times in different areas to account for spatio-temporal variability. However, it is obvious that such an approach is often unrealistic. It is impossible to test all species and ecosystems in the world using such an experimental design. To address this, future ocean acidification research should develop and implement new technology and experimental designs, and elucidate a greater mechanistic understanding at all levels from chemistry to socio-economy.

Single experimental approaches on single organisms often do not capture the true level of complexity of *in situ* marine environments, and multi-disciplinary approaches involving technological advancements and development are critically needed. This includes combining natural variability and monitoring with organismal biology [7]. Below are some examples at differing complexity levels of what we know to date, and what some challenges and focuses are for future research. These are further summarised in Table 6.1.

Ocean acidification at the individual level. Research to date has highlighted individual species variability in response to ocean acidification [8], due in part to differing organismal capacity to tolerate ocean acidification. The capacity for acid-base regulation is an important example, and species that show developed capacity are in general expected to be more resilient to ocean acidification [9,10]. Other studies have demonstrated that tolerance to ocean acidification can even differ between closely related species, or even within species as shown in coccolithophores [11]. Variability within species may indicate the potential for organisms to adapt to ocean acidification, and indeed adaptation has been documented in metazoan species near natural CO_2 vents [12]. Physiological plasticity of organisms and the potential to adapt to changing conditions thus remains an important area for future research [5], further supported by observed long-term acclimatization and adaptation in fast growing microalgae in response to ocean acidification [13]. However, to measure this adaptation potential in all species is unfeasible due to differing

Table 6.1. Some key research gaps and challenges for future ocean acidification research

OA topic area	**Research question(s)**
Biogeochemical processes	Will future OA provide significant feedback to the global carbon cycle and climate change, through global-scale changes in calcification, ocean productivity, particle sinking in the ocean, and effects on other climatically-active gases, e.g. DMS and N_2O? Will the ocean become a less important CO_2 sink in the future, exacerbating atmospheric changes?
Physico-chemical processes	What is the current variability of ocean carbonate chemistry at ecologically-significant temporal and spatial scales, and how will this change under future climate change scenarios, with associated additional changes in temperature, oxygen, stratification, ocean circulation, and river inputs? Which areas of the ocean (e.g. polar regions, upwelling zones, and shelf seas) will experience greatest and most rapid change? Will chemical changes also impact sound transmission in future oceans, with impacts on organism communication [41]?
Physiological and behavioural processes	What are the unifying mechanisms linking species' molecular, metabolic and behavioural responses to ocean acidification? (e.g. based on energy metabolism and acid-base regulation). Does this explain the high taxonomic variability observed in response to OA - and complex interactions with other stressors (e.g. temperature, low oxygen and food/nutrient availability, ultraviolet radiation)? How would different scenarios of ocean acidification affect the immune system resilience of various species to pathogens?
Genetic processes	How can information from relatively short-term studies (weeks to months) on individual species be applied to long-term (decadal), multi-generational responses by populations, involving adaptation and evolution? Does genetic variation confer population resilience? How will this impact marine biodiversity?
Ecological processes	How can experimental studies on OA impacts be best scaled-up to the ecosystem level where interacting multi-species communities are subject to other environmental changes? i.e. allowing for multi-stressor effects, and recognising that negative (or positive) impacts of OA on one species may indirectly benefit (or disadvantage) another and thus community composition and biodiversity. How will impacts on one species impact upon others (trophic interactions), and how will this affect food security through the food chain?
Socio-economic processes	What future socio-economic impacts will arise from ocean acidification? How can we best quantify the risks to non-market ecosystem services (e.g. storm protection provided by tropical coral reefs) as well as to aquaculture and fisheries? Can adaptation strategies be identified for the most vulnerable people and industries? How are various types of communities (from indigenous communities to global markets) differentially vulnerable to the impacts of ocean acidification? How can ocean acidification science best contribute to risk management, the sustainable use of natural resources and national/international policy development?

life history requirements and limitations within laboratory experiments. A key focus for future work may therefore be for taxa and systems involved in ecosystem services; for example coccolithophores [5].

Importantly, organism response to ocean acidification may be different for the short term relative to the long term, or may even differ seasonally as was found in the longest experiment to date (542 days) [3]. Long-term effects of ocean acidification may therefore be buffered or exacerbated at different times of year. Thus while experiments can give us a crucial insight into how organisms respond to ocean acidification, much more may be unaccounted for. Other factors that may lead to variability and hence uncertainty are projected values for temperature, light, salinity and nutrients, and even methodological differences [8]. Light availability is particularly relevant to photosynthetic calcifiers such as tropical coral species, and food availability has been demonstrated to be important in organism response to ocean acidification [14], as well-fed organisms might have more energy to compensate for regulatory changes. Ocean acidification may alter the behaviour (and organism response to) sediment bound metals by altering their bioavailability, as demonstrated by DNA damage and acute toxity in amphipods [15]. This could affect both population and community levels.

Ocean acidification at the population level. To assess the potential impacts of ocean acidification at the population level, it is critical to evaluate different life cycle stages of organisms, such as fertilization, dispersal larval stages and recruitment. To date various studies have demonstrated that early life stages are one of the most vulnerable to ocean acidification. Taking into account that many marine invertebrates show high mortality rate during planktonic larval stages, detrimental impact at these stages can mean critical differences to the population level. A knowledge gap to be addressed across more species and different timescales is the impact of ocean acidification upon gametogenesis. Future work capable of determining the effect of ocean acidification on several life phases, and of subsequent generation of the same species combined with population dynamic models are therefore required. Building on research at different life stages, evolutionary adaptation could be assessed at population levels by correlating ecology, physiology and taxonomy with evolutionary capacity, using known population sizes and recombination rates [5].

Ocean acidification at the community level. The impact of ocean acidification upon species interactions remains relatively unstudied, but is a key area to focus on if whole ecological communities are to be considered [16]. These interactions include changing food quality and how this constrains trophic transfer [17,18], predator-prey relationships [19-21] and feeding rates [22,23]; how the presence of one species (e.g. coralline algae) may directly impact upon the recruitment or success of another (coral juveniles) [24-26]; resource competition [27,28]; and how all the above will have ‘knock on’ effects through competitive interactions [29] and food webs. However, quantifying species interactions will be complicated, as interactions will also be affected by conditioning time, biotic interactions, and initial community compositions [30]. Embedded within this is the need to understand the adaptation potential of different species, and taxa sensitivity to ocean acidification [31]. A number of major experiments have been conducted on pelagic communities over several weeks using mesocosm approaches [32], but there are few such experiments for benthic systems. While mesocosm experiments are an extremely valuable tool for assessing community responses to manipulated variables, there remain scale-dependent challenges in extrapolating results to ecosystems [33].

Ocean acidification at the ecosystem level. Natural volcanic CO_2 vents have provided new insights on the effects of ocean acidification at the ecosystem level, and are a good opportunity to document species-species and species-environments interactions under low pH conditions. These species-environment interactions are very important to consider, as simple impacts upon key species may have cascading effects through the ecosystem [10]. For example, it was demonstrated how ocean acidification can modify the relationship between the burrowing shrimp *Upogebia deltaura* and ammonia oxidising microorganisms inhabiting their burrows, potentially negating positive impacts of shrimp bioturbation[4]. This could impact benthic-pelagic nitrogen cycling, which is fundamental to the food web and the ecosystem dynamics as a whole [4,16]. While these natural systems are extremely useful in the present, further examination of our past (see section 4), can also increase our understanding of how calcifying communities and ecosystems changed under similar past events.

6.2 Theoretical challenges

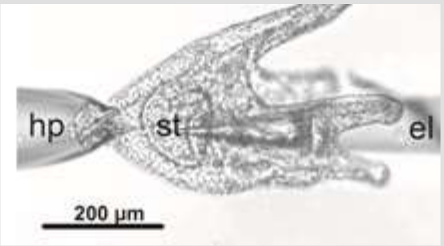
It is impossible to assess the effect of ocean acidification on all species, ecosystems and services. While technology will always be limited when addressing specific research questions, there is one overarching limitation. There is still a lack of theoretical backgrounds and approaches to how the overarching principles of ocean acidification effects can be understood across domains. Conceptual, analytical, and computational models are invaluable to explain pattern in nature. These theoretical frameworks and unifying principles explaining major themes in ocean science (chemistry, physiology, ecology, evolution, multiple stressors, socio-economy, etc.) can assist with prediction and anticipation of local effects of ocean acidification and other drivers.

6.3 Need to prioritize a solution-oriented, multiple drivers approach

Ocean acidification has already begun and can, alone or in combination with other stressors, have significant effects on marine ecosystems and their services to humankind. Ultimately, only the reduction of atmospheric CO_2 levels will alleviate the challenges of ocean acidification and available information should be used to contribute to CO_2 negotiation. In light of the long-term perspective of ocean

Box 6.1. Examples of approaches and technical challenges

Laboratory based perturbation experiments: Understanding of mechanisms in action is needed to improve our predictive power. This will be possible through a better understanding of the biological responses at molecular and physiological levels. This is often associated with technological challenges. For example, new techniques were needed to measure extra and intracellular acid-base regulation and digestion in sea urchin larvae [34,35].



In vivo measurements of larval stomach pH using ion-selective micro-electrodes.

Field based perturbation experiments: Free Ocean CO_2 Enrichment (FOCE) systems have been developed in order to study the effects of ocean acidification on benthic communities by controlling, for several months, the pH to which a natural community is exposed. While the original system was designed for a deployment in the deep-sea, worldwide projects are presently adapting the system to study shallow water areas in temperate and polar environments [36]. The usefulness of this approach was recently demonstrated in a tropical coral reef setting.

The coral proto-free ocean carbon enrichment system (CP-FOCE) deployed on Heron Island, Great Barrier Reef, Australia. Source: David Kline, Scripps.

Field: natural CO_2 vents case studies: From studying ecosystems surrounding natural CO_2 vents it is clear that fundamental changes do happen on the ecosystem level, as calcifying communities may shift to algal-dominant ecosystems [37], undergo a change in species dominance such as in Papua New Guinea [38], or shift community type [39]. A consistent feature of these studies is that species diversity decreases near CO_2 vents. Importantly, natural CO_2 vent ecosystems also include non-calcifying organisms, which could nonetheless play a very important role in species competition and ecosystem function [40].

Left to right: healthy coral reef at Papua New Guinea control site, pH 8.1, unaffected by CO_2 seep; seascape showing moderate seeps, pH 7.8-8.0; and barren seascape showing intense venting of CO_2 and a pH of <7.7, when all coral growth stops. Images courtesy of Katharina Fabricius.

acidification and the millennia it will take to reverse the changes in ocean chemistry, rather than only documenting the disaster, research should also be oriented toward finding solutions. To efficiently prioritize research, sensitivity should be assessed at all levels: (i) chemistry (e.g. regions experiencing the greatest and fasted rapid changes such as polar regions, upwelling zones, and shelf seas) (ii) biology (e.g.

sensitive species or ecosystem, biodiversity at risk, etc.), and (iii) socio-economics (e.g. less developed countries or high dependence of ocean). By improving our understanding of the effects of ocean acidification, we will be able to identify the organisms and ecosystems more at risk that deserve our more urgent attention.

Experiments investigating how biota will respond to ocean acidification have, until recently, largely focused on the manipulation of the carbonate system only. However, marine organisms and ecosystems are increasingly stressed by changes of their physical, chemical and biological environment. For global variables, there has been considerable progress in model projections in the past two years, in conjunction with the preparation of IPCC AR5 report. Bopp et al. [42] used the most recent simulations performed in the framework of the Coupled Model Intercomparison Project 5 to assess how several drivers will evolve during the 21st century. For the "business-as-usual" scenario, the model-mean changes in 2090s (compared to 1990s) for sea surface temperature, sea surface pH and global O_2 content amount to +2.7°C, ~-0.33 pH unit, and -3.5%, respectively. For the "high mitigation efforts now" scenario, corresponding changes are +0.7°C, -0.07 pH unit and -1.8%.

Ocean acidification can interact with other variables synergistically (amplified stress), additively (no additional stress), or antagonistically (reduced stress) [43]. In 2012, only around a third of the 225 papers that reported on the biological response to ocean acidification also manipulated at least one other environmental property. This is a large increase compared to previous years but knowledge on the impacts of multiple drivers is still insufficient to provide reliable projections of biodiversity and ecosystem function. The challenges associated with conducting more complex manipulation experiments that include combined temperature, O_2 stressors, and ultraviolet radiation in conjunction with OA are technological, but also include experimental design (replication vs. regression approach, pseudo-replication, number of treatments for each driver etc.). However, even then, controlled experiments may not capture the full complexity of ecosystems. To fully address the need for multiple driver approaches, comparative ecosystem analyses which combine both experimental observations and models are needed [44].

6.4 Advances in sensing, monitoring, and emerging technologies

Measurements of the pH and the marine carbonate system have traditionally been challenging due to inconsistent pH scales, measurement routines and custom instrumentation that required the expertise and experience of a particular technician to operate. Consequently, inter-comparison exercises between laboratories revealed large discrepancies [45]. Over the last thirty years, great strides have been taken in standardizing our understanding of what exactly the marine carbonate system is, how to measure it and how to report the results, the availability of very high quality reference material, and the standardization of the pH scale for the reporting of ocean acidification – the total hydrogen ion scale [46].

The majority of established long-term ocean acidification time series have used standard, shipboard and laboratory instrumentation for measurements of the four marine carbonate system variables (pH, total alkalinity, total inorganic carbon and the partial pressure (or fugacity) of carbon dioxide in seawater) [47]. Using any two of these variables enables the calculation of the other two, plus the speciation of the marine carbonate system, calcium carbonate saturation states, buffer capacity and the major contributions to the total alkalinity.

As indicated in Section 3, a high density of measurements in both time and space are required if the fine details of local, regional and global ocean acidification are to be routinely identified. New approaches include the adaption of existing techniques, such as ion selective field effect transistors (ISFETs) [48] and the development of approaches to enable remote measurements, thus removing the requirements for an operator. These include measurements from autonomous systems, voluntary observing ships (or ship of opportunity [49]), buoys, profiling floats[50], and wave-riders [51] and landers [52] (Figure 6.1). Adapting these methods have led to the development of novel combinations [53] and lower-cost, low power, long term measurement techniques [54] that are approaching, and sometimes excelling, the accuracy of traditional methods. By incorporating new approaches into the expanding range of monitoring platforms, through initiatives such as GOA-ON (see sections 2 and 3), the current knowledge of natural variability across space and time will be improved, meaning that experimental studies can be better placed into context (natural variability versus projected changes), and future climate change projections will become more accurate.

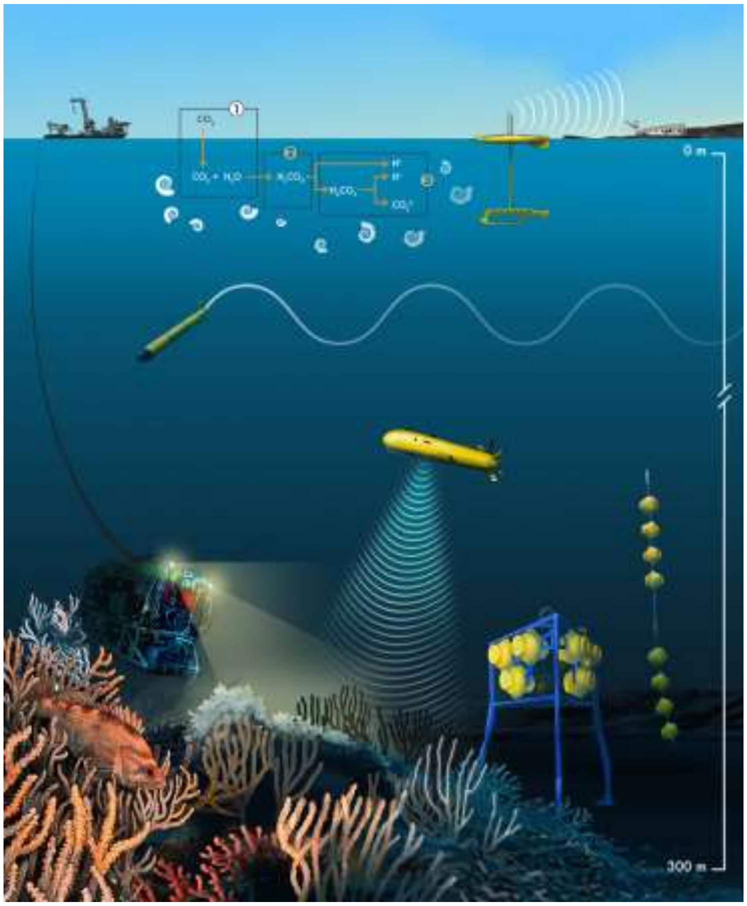


Figure 6.1. A simplified cartoon of various platforms for environmental sensors. These include autonomous and remotely controlled underwater vehicles, wave gliders, moorings and benthic landers. Data from these sensors can be used to to record physical properties of ecosystems. Source: Heriot-Watt University.

1. Dupont S, Portner H (2013) Get ready for ocean acidification. Nature 498: 429-429.
2. Dupont S, Portner HO (2013) A snapshot of ocean acidification research. Marine Biology 160: 1765-1771.
3. Godbold JA, Solan M (2013) Long-term effects of warming and ocean acidification are modified by seasonal variation in species responses and environmental conditions. Philos Trans R Soc Lond B Biol Sci 368: 20130186.
4. Laverock B, Kitidis V, Tait K, Gilbert JA, Osborn AM, et al. (2013) Bioturbation determines the response of benthic ammonia-oxidizing microorganisms to ocean acidification. Philos Trans R Soc Lond B Biol Sci 368: 20120441.
5. Sunday JM, Crim RN, Harley CDG, Hart MW (2011) Quantifying Rates of Evolutionary Adaptation in Response to Ocean Acidification. PLoS ONE 6.
6. McElhany P, Busch DS (2013) Appropriate pCO(2) treatments in ocean acidification experiments. Marine Biology 160: 1807-1812.
7. Hoffmann D, Evans TG, Kelly MW, Padilla-Gamino JL, Blanchette CA, et al. (2014) Exploring local adaptation and the ocean acidification seascape – studies in the California Current Large Marine Ecosystem. Biogeosciences 11: 1053-1064.
8. Wicks LC, Roberts JM (2012) Benthic invertebrates in a high-CO_2 world. Oceanography and Marine Biology: An Annual Review 50: 127-188.
9. Widdicombe S, Spicer J (2008) Predicting the impact of ocean acidification on benthic biodiversity: What can animal physiology tell us? Journal of Experimental Marine Biology and 366: 187-197.

10. Melzner F, Gutowska MA, Langenbuch M, Dupont S, Lucassen M, et al. (2009) Physiological basis for high CO2 tolerance in marine ectothermic animals: pre-adaptation through lifestyle and ontogeny? Biogeosciences 6: 2313-2331.
11. Hoppe CJM, Langer G, Rost B (2011) Emiliania huxleyi shows identical responses to elevated pCO(2) in TA and DIC manipulations. Journal of Experimental Marine Biology and Ecology 406: 54-62.
12. Calosi P, Rastrick SP, Lombardi C, de Guzman HJ, Davidson L, et al. (2013) Adaptation and acclimatization to ocean acidification in marine ectotherms: an in situ transplant experiment with polychaetes at a shallow CO2 vent system. Philos Trans R Soc Lond B Biol Sci 368: 20120444.
13. Benner I, Diner RE, Lefebvre SC, Li D, Komada T, et al. (2013) Emiliania huxleyi increases calcification but not expression of calcification-related genes in long-term exposure to elevated temperature and pCO2. Philos Trans R Soc Lond B Biol Sci 368: 20130049.
14. Edmunds PJ (2011) Zooplanktivory ameliorates the effects of ocean acidification on the reef coral. Limnology 56: 1-11.
15. Roberts DA, Birchenough SNR, Lewis C, Sanders MB, Bolam T, et al. (2013) Ocean acidification increases the toxicity of contaminated sediments. Global Change Biology 19: 340-351.
16. Godbold JA, Calosi P (2013) Ocean acidification and climate change: advances in ecology and evolution. Philos Trans R Soc Lond B Biol Sci 368: 20120448.
17. Branch TA, DeJoseph BM, Ray LJ, Wagner CA (2013) Impacts of ocean acidification on marine seafood. Trends Ecol Evol 28: 178-186.
18. Rossoll D, Bermudez R, Hauss H, Schulz KG, Riebesell U, et al. (2012) Ocean Acidification-Induced Food Quality Deterioration Constrains Trophic Transfer. Plos One 7.
19. Ferrari MCO, Manassa RP, Dixson DL, Munday PL, McCormick MI, et al. (2012) Effects of Ocean Acidification on Learning in Coral Reef Fishes. Plos One 7.
20. Ferrari MCO, McCormick MI, Munday PL, Meekan MG, Dixson DL, et al. (2011) Putting prey and predator into the CO2 equation - qualitative and quantitative effects of ocean acidification on predator-prey interactions. Ecology Letters 14: 1143-1148.
21. Cripps IL, Munday PL, McCormick MI (2011) Ocean Acidification Affects Prey Detection by a Predatory Reef Fish. Plos One 6.
22. Gooding RA, Harley CDG, Tang E (2009) Elevated water temperature and carbon dioxide concentration increase the growth of a keystone echinoderm. Proceedings of the National Academy of Sciences of the United States of America 106: 9316-9321.
23. Kurihara H, Yin R, Nishihara GN, Soyano K, Ishimatsu A (2013) Effect of ocean acidification on growth, gonad development and physiology of the sea urchin Hemicentrotus pulcherrimus. Aquatic Biology 18: 281-292.
24. Albright R, Langdon C (2011) Ocean acidification impacts multiple early life history processes of the Caribbean coral Porites astreoides. Global Change Biology 17: 2478-2487.
25. Doropoulos C, Diaz-Pulido G (2013) High CO2 reduces the settlement of a spawning coral on three common species of crustose coralline algae. Marine Ecology Progress Series 475: 93-99.
26. Doropoulos C, Ward S, Diaz-Pulido G, Hoegh-Guldberg O, Mumby PJ (2012) Ocean acidification reduces coral recruitment by disrupting intimate larval-algal settlement interactions. Ecology Letters 15: 338-346.
27. Tatters AO, Roleda MY, Schnetzer A, Fu F, Hurd CL, et al. (2013) Short- and long-term conditioning of a temperate marine diatom community to acidification and warming. Philos Trans R Soc Lond B Biol Sci 368: 20120437.
28. Tatters AO, Schnetzer A, Fu F, Lie AY, Caron DA, et al. (2013) Short- versus long-term responses to changing CO2 in a coastal dinoflagellate bloom: implications for interspecific competitive interactions and community structure. Evolution 67: 1879-1891.
29. Diaz-Pulido G, Gouezo M, Tilbrook B, Dove S, Anthony KRN (2011) High CO2 enhances the competitive strength of seaweeds over corals. Ecology Letters 14: 156-162.
30. Eggers SL, Lewandowska AM, Ramos JBE, Blanco-Ameijeiras S, Gallo F, et al. (2014) Community composition has greater impact on the functioning of marine phytoplankton communities than ocean acidification. Global Change Biology 20: 713-723.
31. Wittmann AC, Portner H-O (2013) Sensitivities of extant animal taxa to ocean acidification. Nature Climate Change 3: 995-1001.
32. Riebesell U, Czerny J, von Broeckel K, Boxhammer T, Buedenbender J, et al. (2013) Technical Note: A mobile sea-going mesocosm system - new opportunities for ocean change research. Biogeosciences 10: 1835-1847.
33. Gardner RH, Kemp WM, Kennedy VS, Peterson JE, editors (2001) Scaling Relations in Experimental Ecology. New York: Columbia University Press.
34. Stumpp M, Hu M, Casties I, Saborowski R, Bleich M, et al. (2013) Digestion in sea urchin larvae impaired under ocean acidification. Nature Climate Change 3: 1044-1049.
35. Stumpp M, Hu MY, Melzner F, Gutowska MA, Dorey N, et al. (2012) Acidified seawater impacts sea urchin larvae pH regulatory systems relevant for calcification. Proceedings of the National Academy of Sciences of the United States of America 109: 18192-18197.
36. Free Ocean CO2 Enrichment (FOCE) http://www.antarctica.gov.au/about-us/publications/australian-antarctic-magazine/2011-2015/issue-24-june-2013/science/building-a-future-ocean
37. Hall-Spencer JM, Rodolfo-Metalpa R, Martin S, Ransome E, Fine M, et al. (2008) Volcanic carbon dioxide vents show ecosystem effects of ocean acidification. Nature 454: 96-99.
38. Fabricius KE, Langdon C, Uthicke S, Humphrey C, Noonan S, et al. (2011) Losers and winners in coral reefs acclimatized to elevated carbon dioxide concentrations. Nature Climate Change 1: 165-169.
39. Inoue S, Kayanne H, Yamamoto S, Kurihara H (2013) Spatial community shift from hard to soft corals in acidified water. Nature Climate Change 3: 683-687.
40. Connell SD, Kroeker KJ, Fabricius KE, Kline DI, Russell BD (2013) The other ocean acidification problem: CO2 as a resource among competitors for ecosystem dominance. Philosophical Transactions of the Royal Society B-Biological Sciences 368: 20442-20442.
41. Ilyina T, Zeebe RE, Brewer PG (2010) Future ocean increasingly transparent to low-frequency sound owing to carbon dioxide emissions. Nature Geoscience 3: 18-22.
42. Bopp L, Resplandy L, Orr JC, Doney SC, Dunne JP, et al. (2013) Multiple stressors of ocean ecosystems in the 21st century: projections with CMIP5 models. Biogeosciences 10: 6225-6245.
43. Byrne M, Przeslawski R (2013) Multistressor impacts of warming and acidification of the ocean on marine invertebrates' life histories. Integrative and Comparative Biology 53: 582-596.
44. Murawski SA, Steele JH, Taylor P, Fogarty MJ, Sissenwine MP, et al. (2010) Why compare marine ecosystems? Ices Journal of Marine Science 67: 1-9.
45. Poisson A, Culkin F, Ridout P (1990) Intercomparison of CO2 measurements. Deep-Sea Research Part a-Oceanographic Research Papers 37: 1647-1650.
46. Dickson AG, Sabine CL, Christian JR (2007) Guide to best practices for ocean CO2 measurements.: PICES. 191 p.

47. Schuster U, Hannides A, Mintrop L, Koertzinger A (2009) Sensors and instruments for oceanic dissolved carbon measurements. Ocean Science 5: 547-558.
48. Martz TR, Connery JG, Johnson KS (2010) Testing the Honeywell Durafet for seawater pH applications. Limnology and Oceanography: Methods 8: 172-184.
49. Hardman-Mountford NJ (2008) An operational monitoring system to provide indicators of CO2-related variables in the ocean. Ices Journal of Marine Science: 1498-1503.
50. http://www.mbari.org/chemsensor/floatviz.htm
51. Wave Riders http://www.pmel.noaa.gov/co2/story/Carbon+Wave+Glider
52. Gray SEC, DeGrandpre MD, Langdon C, Corredor JE (2012) Short-term and seasonal pH, pCO(2) and saturation state variability in a coral-reef ecosystem. Global Biogeochemical Cycles 26.
53. Easley RA, Patsavas MC, Byrne RH, Liu X, Feely RA, et al. (2013) Spectrophotometric Measurement of Calcium Carbonate Saturation States in Seawater. Environmental Science & Technology 47: 1468-1477.
54. Rerolle VMC, Floquet CFA, Harris AJK, Mowlem MC, Bellerby RRGJ, et al. (2013) Development of a colorimetric microfluidic pH sensor for autonomous seawater measurements. Analytica Chimica Acta 786: 124-131.

7. CONCLUSIONS

The rate of ocean acidification that we have experienced since pre-industrial times, and the projected acidification by the year 2100 is far faster than any similar ocean acidification events in the past 300 million years [1]. As such, current ocean acidification represents a new and unprecedented chapter of marine ecosystem change that could have a significant impact on marine species and ecosystems (including economically important species), on various industries and communities, and on global food security.

From the Paleo-Eocene Thermal Maximum (56 million years ago), believed to be the closest historical analogue to present-day ocean acidification, geological records indicate that a significant number of deep-sea organisms went extinct, and many underwent habitat shifts. The speed at which ocean acidification is currently happening precludes the option of habitat shifts for many benthic species such as shellfish and corals, and may exceed their ability to adapt.

At current rates, aragonite saturation horizons, below which aragonite dissolution occurs, are projected to rise from a few thousand meters to just a few hundred metres in many oceans by the end of the century [2]. If CO_2 emissions continue on a ‘business as usual scenario,’ it is projected that by the end of the century pH will decrease by ~0.33 units and sea surface temperature increase by 2.7°C [3].

Our understanding of ocean acidification and its consequences has increased tremendously in the past 10 years [4], and research to date, from both laboratory and *in situ* work, has highlighted that organism responses to ocean acidification can be very mixed, even between similar species [5]. This variability reflects that some species may be better adapted for projected future conditions than others, but also highlights that experiment length is important as well in determining future long-term responses.

However, some general trends are emerging. Ocean acidification will have a negative effect on calcification or growth at different life cycle stages in many key organisms, such as commercial shellfish, algae important in biogeochemical cycling, and coral reefs [6-10], although adequate food supplies may ameliorate some negative responses [11,12]. It has been demonstrated that most fish are probably able to maintain sufficient oxygen delivery under predicted future CO_2 levels [13], but increased CO_2 can have significant impacts upon fish behaviour [14].

Sensitivity to ocean acidification varies at different life stages, so understanding how negative impacts can “carry-over” [15] from larval to adult stages remains a significant challenge. Ocean acidification is generally detrimental to calcifying larvae [16-18], but non-calcifying larvae are more resilient [19-21]. The impacts of ocean acidification on fertilization success are highly variable, and highlight the potential for selection and genetic adaptation, supporting the concept of ‘winners and losers’ in the face of changing ocean conditions [22,23].

Impacts of ocean acidification will be most keenly and rapidly experienced in the Arctic and Antarctic environments due to their latitudes and low temperatures, and evidence has emerged from a three-year research programme, the Arctic Monitoring and Assessment Programme (AMAP), that acidification will not be uniform across Arctic environments. The research programme also showed that, that while impacts may be positive for some species, other species may face extinction, and that acidification may contribute to an alteration in fish species, with potential impact upon the livelihoods of local communities [24].

When considering how ocean acidification will affect global populations, the response of tropical coral ecosystems to ocean acidification is understandably much scrutinised, as over 400 million people worldwide live within 100km of reefs, and a vast majority rely upon them for their livelihoods and food security [25,26]. The fact that over 95% of the world's calcifying corals currently live above the saturation horizon [27], and that coral growth ceases near natural CO_2 vents [28], indicates that in the long-term, it is not energetically feasible for corals to grow and thrive below the saturation horizon. Any reduction in coral growth (tropical or cold-water) in the future, will have repercussions for the communities that rely upon them.

The economic costs of ocean acidification are only partially known, with many studies focussing on local costs rather than global. However, of the studies that focus on global costs, the impact to molluscs and tropical coral reefs will cost over $1000 billion annually by the end of the century [29,30]. However, these calculations are inherently difficult and are based on what we can currently predict, which largely centre on loss of earnings, and a limited selection of ecosystem services. The actual costs are likely to be in excess of this figure, especially as it only considers ocean acidification, and not potentially compounding factors such as overfishing, sedimentation and temperature rise.

It is important to note that the response to ocean acidification in coastal regions will be influenced by more variable conditions than in the open oceans [31]. As such, varying conditions (exacerbated by diel community metabolism, local phytoplankton blooms and watershed processes) could complicate the predictions we can currently make, and force rapid (relatively) selection of tolerant individuals.

Looking to the immediate future, it is vital to increase our understanding of how multiple stressors will affect marine biodiversity and ecosystems [32], as ocean acidification will be accompanied by changes in oxygen saturation, temperature [3], and ultraviolet radiation in surface waters [33]. Currently, our knowledge on the impacts of multiple drivers is still insufficient to provide reliable projections of biodiversity and ecosystem function and this must be a priority for future work. Increased monitoring capacity is also crucial to understand the current variability in ecosystems and the rate of change they are experiencing. This should include advances in autonomous underwater vehicle (AUV) sensing technology to monitor key benthic and arctic ecosystems currently near to aragonite and calcite saturation horizons.

The incorporation of ocean acidification into governmental planning, environmental conservation and sustainable living has started to accompany growing awareness of the problem [34-36]. This is a very positive step that has been accompanied by several international research consortia involved in addressing key questions to inform policy making decisions. Even if emissions are significantly curtailed now, however, acidification will still last tens of thousands of years. Significant ocean ecosystem change, and learning to live with those changes, therefore seems a certainty.

1. Honisch B, Ridgwell A, Schmidt DN, Thomas E, Gibbs SJ, et al. (2012) The geological record of ocean acidification. Science 335: 1058-1063.
2. Orr JC, Fabry VJ, Aumont O, Bopp L, Doney SC, et al. (2005) Anthropogenic ocean acidification over the twenty-first century and its impact on calcifying organisms. Nature 437: 681-686.
3. Bopp L, Resplandy L, Orr JC, Doney SC, Dunne JP, et al. (2013) Multiple stressors of ocean ecosystems in the 21st century: projections with CMIP5 models. Biogeosciences 10: 6225-6245.
4. Gattuso JP, Hansson L (2011) Ocean Acidification. Oxford: Oxford University Press.
5. Wicks LC, Roberts JM (2012) Benthic invertebrates in a high-CO_2 world. Oceanography and Marine Biology: An Annual Review 50: 127-188.
6. Armstrong RA, Lee C, Hedges JI, Honjo S, Wakeham SG (2002) A new, mechanistic model for organic carbon fluxes in the ocean based on the quantitative association of POC with ballast minerals. Deep-Sea Research Part Ii-Topical Studies in Oceanography 49: 219-236.
7. Klaas C, Archer DE (2002) Association of sinking organic matter with various types of mineral ballast in the deep sea: Implications for the rain ratio. Global Biogeochem Cycles 16: 1116.
8. Erez J, Reynaud S, Silverman J, Schneider K, Allemand D (2011) In: Dubinsky Z, Stambler N, editors. Coral Reefs: an ecosystem in transition.
9. Hoegh-Guldberg O, Mumby P, Hooten A, Steneck R, Greenfield P, et al. (2007) Coral reefs under rapid climate change and ocean acidification. Science 318: 1737.
10. Gazeau F, Parker LM, Comeau S, Gattuso J-P, O'Connor WA, et al. (2013) Impacts of ocean acidification on marine shelled molluscs. Marine Biology 160: 2207-2245.
11. Edmunds PJ (2011) Zooplanktivory ameliorates the effects of ocean acidification on the reef coral. Limnology 56: 1-11.
12. Melzner F, Stange P, Truebenbach K, Thomsen J, Casties I, et al. (2011) Food Supply and Seawater pCO(2) Impact Calcification and Internal Shell Dissolution in the Blue Mussel Mytilus edulis. Plos One 6.
13. Munday PL, McCormick MI, Nilsson GE (2012) Impact of global warming and rising CO2 levels on coral reef fishes: what hope for the future? Journal of Experimental Biology 215: 3865-3873.
14. Munday PL, Pratchett MS, Dixson DL, Donelson JM, Endo GGK, et al. (2013) Elevated CO2 affects the behavior of an ecologically and economically important coral reef fish. Marine Biology 160: 2137-2144.
15. Pechenik JA (1999) On the advantages and disadvantages of larval stages in benthic marine invertebrate life cycles. Marine Ecology Progress Series 177: 269-297.
16. Byrne M (2011) Impact of ocean warming and ocean acidification on marine invertebrate life history stages: vulnerabilities and potential for persistence in a changing ocean. In: Gibson RN, Atkinson RJA, Gordon JDM, editors. Oceanography and Marine Biology: an Annual Review, Vol 49. pp. 1-42.

17. Dupont S, Havenhand J, Thorndyke W, Peck L, Thorndyke M (2008) Near-future level of CO2-driven ocean acidification radically affects larval survival and development in the brittlestar Ophiothrix fragilis. Marine Ecology Progress Series 373: 285-294.
18. Byrne M, Ho M, Wong E, Soars NA, Selvakumaraswamy P, et al. (2011) Unshelled abalone and corrupted urchins: development of marine calcifiers in a changing ocean. Proceedings of the Royal Society B-Biological Sciences 278: 2376-2383.
19. Dupont S (2010) Near future ocean acidification increases growth rate of the lecithotrophic larvae and juveniles of the sea star Crossaster papposus. Journal of Experimental ….
20. Byrne M, Gonzalez-Bernat M, Doo S, Foo S, Soars N, et al. (2013) Effects of ocean warming and acidification on embryos and non-calcifying larvae of the invasive sea star Patiriella regularis. Marine Ecology Progress Series 473: 235-+.
21. Chua CM, Leggat W, Moya A, Baird AH (2013) Temperature affects the early life history stages of corals more than near future ocean acidification. Marine Ecology Progress Series 475: 85-92.
22. Foo SA, Dworjanyn SA, Poore AGB, Byrne M (2012) Adaptive Capacity of the Habitat Modifying Sea Urchin Centrostephanus rodgersii to Ocean Warming and Ocean Acidification: Performance of Early Embryos. Plos One 7.
23. Schlegel P, Havenhand JN, Gillings MR, Williamson JE (2012) Individual Variability in Reproductive Success Determines Winners and Losers under Ocean Acidification: A Case Study with Sea Urchins. Plos One 7.
24. Arctic Monitoring and Assessment Programme. Oslo, Norway.http://www.amap.no/documents/doc/AMAP-Arctic-Ocean-Acidification-Assessment-Summary-for-Policy-makers/808
25. Teh LSL, Teh LCL, Sumaila UR (2013) A Global Estimate of the Number of Coral Reef Fishers. Plos One 8.
26. Donner SD, Potere D (2007) The inequity of the global threat to coral reefs. Bioscience 57: 214-215.
27. Guinotte JM, Orr JC, Cairns S, Freiwald A, Morgan L, et al. (2006) Will human-induced changes in seawater chemistry alter the distribution of deep-sea scleractinian corals? Frontiers in Ecology and the Environment 4: 141-146.
28. Fabricius KE, Langdon C, Uthicke S, Humphrey C, Noonan S, et al. (2011) Losers and winners in coral reefs acclimatized to elevated carbon dioxide concentrations. Nature Climate Change 1: 165-169.
29. Brander L.M., Narita D, Rehdanz K, Tol RSJ (In press) The economic impact of ocean acidification. In: Paulo A.L.D., Nunes PALD, P. K, T. D, editors. Economics of biodiversity and ecosystem services: Edward Elgar.
30. Cooley SR, Lucey N, Kite-Powell H, Doney SC (2012) Nutrition and income from molluscs today imply vulnerability to ocean acidification tomorrow. Fish and Fisheries 13: 182-215.
31. Duarte CM, Hendriks IE, Moore TS, Olsen YS, Steckbauer A, et al. (2013) Is Ocean Acidification an Open-Ocean Syndrome? Understanding Anthropogenic Impacts on Seawater pH. Estuaries and Coasts 36: 221-236.
32. Noone KJ, Sumaila UR, Diaz RJ (2013) Managing ocean environments in a changing climate: sustainability and economic perspectives: Elsevier.
33. IGBP, IOC, SCOR (2013) Ocean Acidification Summary for Policymakers – Third Symposium on the Ocean in a High-CO2 World. International Geosphere-Biosphere Programme. Stockolm, Sweden
34. Logan C (2010) A Review of Ocean Acidification and America’s Response. Bioscience 60: 819-828.
35. Fauville G, Saljo R, Dupont S (2013) Impact of ocean acidification on marine ecosystems: educational challenges and innovations. Marine Biology 160: 1863-1874.
36. Pope A, Selna E (2013) Communicating Ocean Acidification. Journal of Museum Educations 38: 279-285.

Annex

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