CHAPTER 15

Ocean acidification: knowns, unknowns, and perspectives

Jean-Pierre Gattuso, Jelle Bijma, Marion Gehlen, Ulf Riebesell, and Carol Turley

15.1 Introduction

Although the changes in the chemistry of seawater driven by the uptake of $\text{CO}_2$ by the oceans have been known for decades, research addressing the effects of elevated $\text{CO}_2$ on marine organisms and ecosystems has only started recently (see Chapter 1). The first results of deliberate experiments on organisms were published in the mid 1980s (Agegian 1985) and those on communities in 2000 (Langdon et al. 2000; Leclercq et al. 2000). In contrast, studies focusing on the response of terrestrial plant communities began much earlier, with the first results of free-air $\text{CO}_2$ enrichment experiments (FACE) being published in the late 1960s (see Allen 1992). Not surprisingly, knowledge about the effects of elevated $\text{CO}_2$ on the marine realm lags behind that concerning the terrestrial realm. Yet ocean acidification might have significant biological, ecological, biogeochemical, and societal implications and decision-makers need to know the extent and severity of these implications in order to decide whether they should be considered, or not, when designing future policies.

The goals of this chapter are to summarize key information provided in the preceding chapters by highlighting what is known and what is unknown, identify and discuss the ecosystems that are most at risk, as well as discuss prospects and recommendation for future research.

15.2 Knowns and unknowns

The chemical, biological, ecological, biogeochemical, and societal implications of ocean acidification have been comprehensively reviewed in the previous chapters with one minor exception. Early work has shown that ocean acidification significantly affects the propagation of sound in seawater and suggested possible consequences for marine organisms sensitive to sound (Hester et al. 2008). However, subsequent studies have shown that the changes in the upper-ocean sound absorption coefficient at future $\text{pH}$ levels will have no or a small impact on ocean acoustic noise (Joseph and Chiu 2010; Udovydenkov et al. 2010).

The goal of this section is to condense the current knowledge about the consequences of ocean acidification in 15 key statements (Table 15.1). Each statement is given levels of evidence and, when possible, a level of confidence as recommended by the Intergovernmental Panel on Climate Change (IPCC) for use in its 5th Assessment Report (Mastrandrea et al. 2010). For the sake of brevity, the sections below do not provide the bibliographic citations which have already been given in the other chapters of this book. Readers are invited to refer to the relevant chapters indicated in Table 15.1 for a complete list of supporting references.

15.2.1 Chemical aspects

15.2.1.1 Ocean acidification occurred in the past

It is known with a very high level of confidence that ocean acidification occurred in the past. On geological timescales, the $\text{CO}_2$ concentration in the atmosphere and the carbonate chemistry of the oceans are constantly changing and adjusting to the forcings of tectonics, volcanism, weathering, biology, and, currently, human activity. Note, however, that atmospheric $p\text{CO}_2$ alone does not tell us much about the
Table 15.1  Summary of the knowns, unknowns, and challenges related to ocean acidification. The recommendations of Mastrandrea et al. (2010) were used for the levels of evidence (‘limited’, ‘medium’, or ‘robust’) and confidence (‘very low’, ‘low’, ‘medium’, ‘high’, and ‘very high’). For statements related to projected impacts of anthropogenic ocean acidification, ranges of $\rho$CO$_2$, pH, CaCO$_3$ saturation state, etc. projected for 2100 under business-as-usual CO$_2$ emissions (e.g. generating atmospheric CO$_2$ concentrations of 793 ppmv in 2100) are considered. Question marks indicate that the effect is unknown. The chapters in which detailed information can be found are indicated.

<table>
<thead>
<tr>
<th>Statement</th>
<th>Level of evidence</th>
<th>Level of confidence</th>
<th>Challenges</th>
<th>Chapter(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Chemical aspects</strong></td>
<td></td>
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<tr>
<td>Ocean acidification occurred in the past</td>
<td>Robust</td>
<td>Very high</td>
<td>Better constrain palaeoreconstructions of the carbonate system</td>
<td>2, 3</td>
</tr>
<tr>
<td>Ocean acidification is in progress</td>
<td>Robust</td>
<td>Very high</td>
<td>Better monitoring of key areas (e.g. coastal sites, coral reefs, polar regions, and the deep sea)</td>
<td>1, 3</td>
</tr>
<tr>
<td>Ocean acidification will continue at a rate never encountered in the past 55 Myr</td>
<td>Robust</td>
<td>Very high</td>
<td>Find two independent carbonate chemistry proxies to reconstruct the ocean carbonate chemistry with a high degree of confidence</td>
<td>2, 3</td>
</tr>
<tr>
<td>Future ocean acidification depends on emission pathways</td>
<td>Robust</td>
<td>Very high</td>
<td>Improve the representation of physical regimes at the regional scale to derive regional estimates</td>
<td>3, 14</td>
</tr>
<tr>
<td>The legacy of historical fossil fuel emissions on ocean acidification will be felt for centuries</td>
<td>Robust</td>
<td>Very high</td>
<td>Improve the representation of physical regimes at the regional scale to derive regional estimates</td>
<td>14</td>
</tr>
<tr>
<td><strong>Biological and biogeochemical responses</strong></td>
<td></td>
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<tr>
<td>Ocean acidification will adversely affect calcification</td>
<td>Medium</td>
<td>High</td>
<td>Determine the mechanisms explaining that a few calcifiers are not affected or stimulated. Gain field evidence in addition to that available from CO$_2$ vents. Identify approaches to improve attribution on field observations</td>
<td>4, 6, 7</td>
</tr>
<tr>
<td>Ocean acidification will stimulate primary production</td>
<td>Medium</td>
<td>High</td>
<td>More work needed at the community level and under field conditions to better assess the global magnitude of the response</td>
<td>6, 7</td>
</tr>
<tr>
<td>Ocean acidification will stimulate nitrogen fixation</td>
<td>Medium</td>
<td>Medium</td>
<td>Investigate more species to test whether it is a widespread response. Determine the interaction with other variables in order to better assess the global magnitude and biogeochemical consequences</td>
<td>6</td>
</tr>
<tr>
<td>Some species or strains are tolerant</td>
<td>Robust</td>
<td>Very high</td>
<td>Gain a better understanding of the molecular and biochemical mechanisms underlying processes such as calcification</td>
<td>6, 7</td>
</tr>
<tr>
<td>Some taxonomic groups will be able to adapt</td>
<td>Limited</td>
<td>?</td>
<td>Identify approaches and tools to estimate the adaptation potential</td>
<td>4, 5, 6, 7, 8</td>
</tr>
<tr>
<td>Ocean acidification will change the composition of communities</td>
<td>Robust</td>
<td>High</td>
<td>Collect better information on non-calcifiers in the palaeorecord and determine the magnitude of the change in present key ecosystems</td>
<td>4, 5, 6, 7, 9, 10</td>
</tr>
<tr>
<td>Ocean acidification will impact food webs and higher trophic levels</td>
<td>Limited</td>
<td>?</td>
<td>Determine how species that may disappear will be replaced and whether the nutritional value of the replacement species may change</td>
<td>6, 7</td>
</tr>
<tr>
<td>Ocean acidification will have biogeochemical consequences at the global scale</td>
<td>Medium</td>
<td>Medium</td>
<td>A better understanding of key processes as a function of carbonate system variables is critically needed to improve model parameterization</td>
<td>11, 12</td>
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(continued)
satisfaction state of the ocean with respect to CaCO₃, as two parameters of the carbonate system are required to determine the seawater carbonate chemistry (see Box 1.1 in Chapter 1). There have been periods in earth’s history during which the ocean had a lower pH than today (see Chapters 2 and 4), for instance at the end of the Permian 251 Myr ago, at the Palaeocene–Eocene Thermal Maximum (PETM) 55 Myr ago, and during the deglaciations that are characteristic of the Pleistocene epoch (which started ~1.8 Myr ago and ended 10 kyr ago, with the beginning of the Holocene). These events were a consequence of perturbations of the carbon cycle of different sizes, origins, and rates. The average saturation state with respect to CaCO₃ of surface waters was still favourable to calcifiers despite high CO₂ levels, due to higher concentrations of calcium and/or higher total alkalinity than today. In other words, pH and saturation state were decoupled during these events whereas both are declining together in the Anthropocene (the geological epoch that serves to mark the recent extent of human activities that have had a significant global impact on the earth’s ecosystems).

All past ocean acidification events were accompanied by global warming, stronger stratification of the water column, and a decrease in the oxygenation of the deep sea. Attribution of the biological responses to one or several of these environmental factors is therefore difficult. It is important to realize that the climatic conditions prior to each of the events were very different from today (initial CO₂, ocean temperature, and chemistry). However, the most important difference between all previous geological events compared with that of the Anthropocene is the rate at which the human-induced carbon perturbation is proceeding (see Section 15.2.1.2).

Even though there is no perfect analogue to the present carbon perturbation, one should expect that the consequences of anthropogenic ocean acidification can only be worse than those recorded in the geological records, simply because the rate of change is unprecedented in the earth’s history and marine ecosystems as we know them today have mainly evolved during a time of low atmospheric CO₂ and well-buffered seawater. The most pressing challenge remains to find two independent carbonate chemistry proxies that will allow us to reconstruct the ocean carbonate chemistry during earth’s history.

### Table 15.1 Continued

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<thead>
<tr>
<th>Statement</th>
<th>Level of evidence</th>
<th>Level of confidence</th>
<th>Challenges</th>
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</thead>
<tbody>
<tr>
<td>Policy and socio-economic aspects</td>
<td></td>
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<tr>
<td>There will be socio-economic consequences</td>
<td>Limited</td>
<td>?</td>
<td>Quantifying the monetary value of the goods and services that oceans provide and assessing how these may be impacted by ocean acidification</td>
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<tr>
<td>An ocean acidification threshold that must not be exceeded can be defined</td>
<td>Limited</td>
<td>?</td>
<td>Initiate and sustain an international effort to compile the increasing number of data being published in order to defined threshold(s). Investigate the need to consider thresholds based on geographical location, species, and ecosystems to advise decision-makers</td>
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15.2.1.2 Ocean acidification is in progress

It is known with a very high level of confidence that ocean acidification has been in progress since the beginning of the Industrial Revolution. The evidence is robust and comes from modelling but also from time-series stations and repeat measurements (see Chapter 3). Despite the short duration of the time series, the relatively short time interval between repeat measurements and a large seasonal variability in some sites, the decrease in pH and carbonate ion concentration and the increase in the concentration of dissolved inorganic carbon and pCO₂ are statistically significant. The decline in pH ranges from ~0.0017 to ~0.0019 units yr⁻¹ in the surface waters of the open-ocean stations. The evidence is not as extensive in marginal seas, mostly because
there are very few high-quality datasets covering a time span long enough to distinguish the declining trend against a seasonal and interannual variability which are much larger than in the open ocean. However, in Chapter 3, using an equilibrium approach and reasonable assumptions, Orr demonstrates that the changes of pH in marginal seas are generally within 10% of those of the open ocean. The situation is considerably more complex in the nearshore coastal ocean where pH is not only controlled by CO$_2$ uptake but also by changes in hydrodynamics and in the inputs of freshwater and organic matter. Nevertheless, it is certain that the uptake of anthropogenic CO$_2$ forces coastal systems towards a lower pH. Although ocean acidification is well documented in temperate oceanic waters, relatively little is known in the high latitudes, deep ocean, coastal areas, and marginal seas. A future challenge is to establish time-series measurements in these areas, not only to improve our understanding of present-day variability but also to help improve future projections.

15.2.1.3 Ocean acidification will continue at a rate never encountered in the past 55 Myr
The coupling between pH and the saturation state with respect to CaCO$_3$ ($\Omega$) depends on both the magnitude and rate of CO$_2$ release (see Chapter 2). $\Omega$ is quite tightly regulated in a well-buffered ocean, even when pH changes. Two processes control $\Omega$ at different timescales: the dissolution of carbonate sediment (‘seafloor carbonate neutralization’ with a timescale of about 2 kyr) and rock weathering (‘terrestrial carbonate neutralization’ with a timescale of about 8 kyr; Ridgwell and Hargreaves 2007).

Releasing CO$_2$ over timescales shorter than ~1 kyr, as is happening today, is too fast for the two compensatory mechanisms to operate; consequently, $\Omega$ and pH decline in concert. The release of CO$_2$ on a timescale of ~2 kyr results in a partial buffering by seafloor carbonate neutralization and a partial decoupling of pH and $\Omega$. On timescales longer than 10 kyr, $\Omega$ is more or less regulated, but the impacts of changes in climate and ocean circulation still need to be explored.

The carbon perturbation is estimated to have been of the order of 0.3 to 0.5 Gt C yr$^{-1}$ (Kump et al. 2009) during the end Permian mass extinction. For the PETM, the closest analogue to the ongoing ocean acidification, estimates vary but a minimum value of 0.6 Pg C yr$^{-1}$ during 5–10 kyr has been proposed (Zeebe et al. 2009). These past emissions are dwarfed by the current emissions of roughly 8.4 Pg C yr$^{-1}$ (Friedlingstein et al. 2010) which are so large that the natural compensatory mechanisms cannot operate. Today’s ocean is therefore slave to the atmosphere and its uptake of CO$_2$ is outstripping the buffering capacity of seawater, leading to a tight coupling between pH and $\Omega$ which decrease in concert. It is with a very high level of confidence that one can conclude that the current ocean acidification event is occurring on a timescale much faster than during the PETM and could therefore have more serious consequences. It is also worth mentioning that full chemical recovery after the PETM perturbation took about 100,000 yr. As already mentioned before, the most pressing challenge remains to find two independent carbonate chemistry proxies that will allow us to reconstruct the ocean carbonate chemistry during earth’s history.

15.2.1.4 Future ocean acidification depends on emission pathways
Models project important changes in carbonate chemistry in response to historical and 21st century CO$_2$ emissions scenarios such as those selected for the 4th and 5th Assessment Reports of the IPCC (see Chapter 14). It is known with a very high level of confidence that future ocean acidification will depend on the emission pathways considered. The global surface-ocean mean $\Omega_a$ (global average saturation state of surface waters with respect to aragonite) is projected to decrease between 0.9 and 1.4 units from pre-industrial time to the end of the present century, while the corresponding change in pH ranges between 0.21 and 0.36 units. These changes in the global-mean properties such as $\Omega_a$ and pH hide large regional differences. Models project imminent undersaturation of surface waters in the Arctic ocean. Over 50% of the surface waters of the Arctic Ocean are projected to become undersaturated at atmospheric CO$_2$ levels exceeding 490 ppmv. Undersaturation of surface waters is also projected to be reached for atmospheric CO$_2$ levels exceeding 580 ppmv in the Southern Ocean. The overall largest changes in $\Omega_a$ are predicted for the tropics and
Mitigation leads to lower levels of atmospheric CO$_2$ and hence less climate change and ocean acidification. Global surface-ocean mean $\Omega_a$ decreases between 0.1 to 0.8 and pH decreases by 0.04 to 0.19 units. Mitigation options that lower atmospheric CO$_2$ will thus effectively alleviate the impacts of ocean acidification on marine systems. Due to the inertia of the earth system, the benefits from early mitigation of atmospheric CO$_2$ increase will become increasingly important after 2100. The main shortcoming of present coupled climate–carbon cycle models is their coarse resolution and over-simplistic representation of biological processes. This makes it difficult to evaluate different emission pathways and mitigation options at the regional scale and in particular in terms of biological impacts.

15.2.1.5 The legacy of historical and 21st century fossil fuel emission will be felt for centuries

It is known with a very high level of confidence that the legacy of historical and 21st century fossil fuel emission will be felt for centuries. Coupled climate–carbon cycle models are typically used to explore the long-term commitment to ocean acidification caused by the uptake of CO$_2$ since the onset of industrialization and over the 21st century following different emission scenarios. To this end, emissions are unrealistically set to zero in the year 2000 (historical scenario) or in 2100 for scenarios of the IPCC SRES B1 (low) and A2 (high) to explore the legacy of past emissions (see Chapter 14). For atmospheric CO$_2$ levels peaking around 850 ppmv (high scenario), $\Omega_a$ decreases by 50% in 2100. It increases subsequently as emissions are set to zero, but remains substantially lower than the pre-industrial value until the year 2500. Atmospheric CO$_2$ falls below 350 ppmv within a few decades in the historical scenario, and the perturbation of ocean chemistry remains relatively small. While the surface-ocean carbonate system responds quickly to changes in atmospheric CO$_2$ through air–sea gas exchange, the interior of the ocean shows a delayed response due to the centennial timescales involved in the surface-to-deep transport of anthropogenic CO$_2$. In the high scenario, the volume occupied by undersaturated water increases from 60% in pre-industrial times to 75% in 2100 and reaches a maximum of 90% in 2300, 200 yr after the emissions are set to zero. The volume of undersaturated water increases up to 83% in the low scenario. Changes projected for the historical scenario are much more modest, yet the volume of supersaturated waters decreases too. These drastic and lasting changes in deep-water carbonate chemistry suggest the loss of suitable habitats for calcifying organisms.

Past and 21st century CO$_2$ emissions set the extent of ocean acidification over the coming centuries. Due to the inertia in the earth system, impacts of CO$_2$ emissions on seawater carbonate chemistry are delayed and will continue to perturb the biogeochemical cycles and marine ecosystems for centuries to come.

As mentioned in the previous section, the main shortcoming of present coupled climate–carbon cycle models for evaluating future changes in ocean carbonate chemistry is their coarse resolution. These models converge in their projections of the chemical consequences of ocean acidification at global as well as basin scale. However, studies mostly report changes in the mean state of properties (e.g. mean surface-ocean pH or saturation state averaged over a year or a decade). In order to integrate modelling studies with the growing understanding of the differential response of contrasting ocean regions, future research will need to focus on the assessment of impacts of ocean acidification at the regional scale. The interplay between ocean physics, chemistry, and biology will need to be investigated at seasonal and interannual timescales.

15.2.2 Biological and biogeochemical responses

15.2.2.1 Ocean acidification will adversely affect calcification

The precipitation, dissolution, and preservation of CaCO$_3$ are the processes which have been investigated most in the context of ocean acidification, both in the fossil record and in perturbation experiments. In Chapter 4 Knoll and Fischer provide an overview of the fate of calcifiers during earth’s history. They show that several events in the geological
past bearing the fingerprint of ocean acidification, global warming, and expanding anoxia, led to devastating changes in the abundance, diversity, and evolution of calcifying organisms. The bottom line from geological history is that the rate of the carbon perturbation is the key to the response of calcifying organisms (see Chapter 2 and above) as well as its amplification by global warming and declining levels of dissolved oxygen.

Despite the fact that some perturbation experiments reported no effect or a positive effect of ocean acidification on the rate of calcification of a few organisms (reviewed in Chapters 6 and 7), meta-analyses reveal an overall significant negative effect (Kroeker et al. 2010). The mean effect is negative and significant on corals, negative with a similar magnitude but non-significant on calcifying algae, coccolithophores, and molluscs, positive and significant on crustaceans, and positive but non-significant on echinoderms. Whether or not calcification decreases in response to elevated CO\(_2\) and lower Ω, the deposition of CaCO\(_3\) is thermodynamically less favourable under such conditions. Some organisms may have the capacity to up-regulate their metabolism and calcification to compensate for lower Ω. However, this would have energetic costs that would divert energy from other essential processes, and thus would not be sustainable in the long term. Full or partial compensation may be possible in certain organisms if the additional energy demand required to calcify under elevated CO\(_2\) can be supplied as food, nutrients, and/or light (for those organisms dependent on photosynthesis).

Overall, calcifiers precipitating the less soluble aragonite and low-magnesian calcite are negatively affected, whereas those precipitating the more soluble high-magnesian calcite are not significantly affected. This may indicate that biological control of calcification is more important than the solubility of the mineral precipitated (Kroeker et al. 2010) but it seems that the analysis is flawed (Anderson, pers. comm.). Interestingly, Kroeker et al. (2010) found that calcifying organisms are more susceptible overall to ocean acidification than non-calcifying organisms across other processes.

Overall, the level of evidence that ocean acidification will adversely affect calcification is medium and the confidence level high. The remaining challenges are to estimate the energetic and physiological trade-offs in all life stages, and to improve our knowledge about the molecular and physiological mechanisms involved in calcification in order to better understand how the direction and magnitude of the response to ocean acidification are controlled.

15.2.2.2 Ocean acidification will stimulate primary production

In the oceans, photosynthesis is carried out primarily by microscopic phytoplankton, and to a lesser extent by macroalgae and seagrasses. Photosynthetic organisms must acquire inorganic carbon and a suite of major and trace nutrients from surface seawater. Dissolved CO\(_2\), rather than the much more abundant bicarbonate ion, is the substrate used in the ‘carbon fixation’ step of photosynthesis. The enzyme responsible for carbon fixation, ribulose-1, 5-bisphosphate carboxylase oxygenase (RubisCO), has a low substrate affinity, achieving half-saturation of carbon fixation at concentrations well above those present in seawater. CO\(_2\) must therefore be concentrated at the site of fixation against a concentration gradient and therefore with an energetic cost. As CO\(_2\) diffuses readily through biological membranes, a large portion of the CO\(_2\) transported into photosynthetic organisms is lost again via leakage. It is conceivable, therefore, that an increase in seawater CO\(_2\) concentration reduces leakage and lowers the cost of concentrating CO\(_2\), thereby stimulating primary production.

Stimulating effects of elevated CO\(_2\) on photosynthesis and carbon fixation have indeed been observed in a variety of phytoplankton taxa, including diatoms, coccolithophores, cyanobacteria, and dinoflagellates. Modest increases of 10–30% in photosynthetic carbon fixation in response to elevated CO\(_2\) were also observed in bioassay studies with oceanic plankton assemblages as well as in mesocosm experiments with coastal plankton communities. The extent to which phytoplankton respond to increased CO\(_2\) depends to a large extent on the physiological mechanisms of inorganic carbon uptake and intracellular assimilation. Marine primary producers encompass phylogenetically very diverse groups, from prokaryotes to angiosperms, differing widely in their photosynthetic apparatus and carbon-concentrating mechanisms (CCMs). Species with effective CCMs are likely to be less sensitive to increased CO\(_2\) levels than those lacking
efficient CCMs. These differences are likely to alter competitive relationships among phytoplankton groups and result in shifts in plankton species composition as the oceanic CO$_2$ concentration continues to rise. The level of confidence of this stimulating effect is medium and its magnitude must be better constrained, especially at community level under in situ conditions.

15.2.2.3 Ocean acidification will stimulate nitrogen fixation

The fixation of atmospheric nitrogen gas (N$_2$) into ammonium (NH$_4^+$), a form readily available to the biota, is carried out by a small group of diazotrophic cyanobacteria. This process represents a major input of ‘new’ nitrogen to oligotrophic marine ecosystems. Because large parts of the global ocean are nitrogen-limited, nitrogen fixation plays a key role in determining primary production of the world’s oceans. It is an energetically costly process which also requires the synthesis of a complex iron-rich enzyme. Additionally, cyanobacteria have to invest heavily in concentrating CO$_2$ at the site of carboxylation due to the low affinity of their RubisCO. Increasing surface-ocean CO$_2$ concentrations may therefore be beneficial for diazotrophic cyanobacteria. If the energy saved in the carbon acquisition process is reallocated to other processes, elevated CO$_2$ could stimulate nitrogen fixation (see Chapter 6). Enhanced nitrogen fixation in response to elevated CO$_2$ was indeed observed in the abundant filamentous diazotroph *Trichodesmium* sp. as well as the unicellular species *Crocosphaera watsonii* under iron-replete conditions. No stimulation was observed for *Nodularia* spumigena, a heterocystous diazotrophic cyanobacterium common in the Baltic Sea.

The level of confidence that ocean acidification will stimulate nitrogen fixation is medium because, considering the potential phylogenetic and metabolic diversity of marine nitrogen fixers, it is currently difficult to determine the representativeness for the global ocean of laboratory results on two of the three species investigated so far. Moreover, because of the high demand for iron and energy, the ecological niche of diazotrophs is restricted to iron-rich, nitrogen-poor waters in areas, or during periods of, high solar irradiance. With little information on the synergistic effects of CO$_2$, light, and iron, and a small number of species tested so far, it is too early to assess the global significance of a stimulating effect of rising CO$_2$ on oceanic nitrogen fixation.

15.2.2.4 Some species or strains are tolerant

It is known with a very high level of confidence that some species or strains are tolerant to ocean acidification. Tolerance to ocean acidification in the range projected for the next century varies greatly among phyla and even species and is largely determined by the mechanisms and capacities of acid–base regulation. In metazoans, this is linked to the metabolic rate and, in turn, to the transport capacities for oxygen and CO$_2$. Several groups of animals (e.g. mammals, fishes, and some molluscs) with a high capacity for oxygen and CO$_2$ transport and exchange appear to be tolerant of lower pH, at least over short periods such as those of intense activity. In contrast, most marine invertebrate taxa have less developed gas exchange and acid–base regulatory capacities, and appear to have a lower tolerance to ocean acidification. Tolerance levels are also likely to be lower in early life stages, e.g. during egg and larval development.

In autotrophic organisms CO$_2$/pH sensitivity is linked to the carbon acquisition mechanisms supplying inorganic carbon to photosynthesis and, in the case of calcareous autotrophs, also to calcification. Differences in CO$_2$/pH sensitivity exist, for example, between diatoms, coccolithophores, and cyanobacteria, partly related to the efficiency of their CO$_2$ concentrating mechanisms. Different tolerances are also observed between species of the same group, or even strains of the same species, as seen for example in coccolithophores. To what extent these differences will affect overall competitive fitness and lead to the replacement of CO$_2$/pH-sensitive species by tolerant ones is currently unknown.

15.2.2.5 Some taxonomic groups will be able to adapt

Changes in environmental conditions generate two types of responses (Bradshaw and Holzapfel 2006): phenotypic plasticity, the ability of individuals to modify their behaviour, morphology, or physiology, and genetic (evolutionary) changes. Phenotypic plasticity is well known, but genetic changes have also been observed in populations of animals as diverse as birds, squirrels, and mosquitoes in response to the environmental changes that have
occurred in the past decades. When the rate of environmental change in the geological record is fast, the probability of extinction is increased, suggesting that adaptation to slower changes is possible. Our understanding of the sensitivity of marine organisms to ocean acidification is almost entirely based on short-term perturbation experiments, lasting between a few hours and a few weeks. The results of such studies provide valuable insights into the phenotypic response of test organisms and communities to ocean acidification. However, such studies are generally too short to allow for evolutionary adaptation.

Ocean acidification occurs gradually over timescales of decades to centuries. With generation times of hours to days, unicellular algae and bacteria will go through tens of thousands of generations as $pCO_2$ increases to projected maximum levels, which may be sufficient for adaptive processes to become relevant. Moreover, most studies so far have focused only on selected phases of test organisms’ life cycles. An individual may experience very different environmental conditions at different stages during its life cycle and its potential to adapt to stresses is likely to vary over different developmental phases.

The potential for adaptation can be investigated experimentally in studies using long-term exposure to elevated CO$_2$. This approach is most promising for organisms with short generation times, such as autotrophic and heterotrophic microorganisms. Adaptation potential can also be deduced from in situ observations at natural CO$_2$ venting sites, where benthic marine communities have experienced high $pCO_2$ and low pH conditions for several centuries or millennia. While this approach provides some valuable information on the potential range of adaptive responses at the organism, community, and ecosystem levels, the extrapolation of the observed responses to future ocean acidification is complicated for a number of reasons. The fact that $pCO_2$ and pH levels at these sites strongly vary over time and space (e.g. depending on water currents) and often exceed values projected for the next centuries makes it impossible to determine a dose–response relationship. As many benthic organisms are motile or have pelagic life stages, it is also difficult to distinguish between the local community, which has gone through multiple generations at the venting site, and those individuals which have recently invaded the area. Apart from CO$_2$ venting sites, areas regularly experiencing upwelling of CO$_2$-enriched deep waters provide another natural laboratory for studying adaptation potential. While studies at these sites are facing some of the same difficulties as those at CO$_2$ venting sites (e.g. continuous invasion of non-exposed individuals), the range of $pCO_2$ is usually smaller, with less uncertainty regarding the dose–response relationship. Adaptation potential, or the lack thereof, can also be deduced from species extinction during high-CO$_2$ events during earth’s history. A major difficulty lies in the uncertainty about whether these events provide a reasonable analogue for ocean acidification in the Anthropocene (see Chapters 2 and 4). In summary, the level of evidence that some species will adapt is limited. Due to the important role that adaptive processes may have on the response of the biota to ocean acidification, it is crucial to make the best use of all available approaches for addressing this critical issue.

15.2.2.6 **Ocean acidification will change the composition of communities**

Ecosystems are structured by the physico-chemical environment, including light, temperature, oxygen conditions, availability of nutrients and food, energy input to the mixed layer or, for benthic systems, substrate stability and heterogeneity. Ocean acidification directly modifies the chemical boundary conditions of marine communities and, in synergy with climate change, might result in the reorganization of certain marine ecosystems. For example, the poleward migration of species (Fields et al. 1993) could be impaired because ocean acidification will be particularly strong at high latitudes. The differential response of organisms to changes in carbonate chemistry is likely to modify the composition of communities through species loss and migration, changes in species succession, or, more generally, through altered competition between species.

Evidence for changes in community composition in response to ocean acidification is still scarce. However, comparative analysis of shallow-water benthic communities in the vicinity of volcanic CO$_2$ vents in the Mediterranean Sea demonstrates a 30% decrease in the overall diversity as well as a decrease
in abundance or the loss of benthic calcifiers at lower pH. Similarly, changes in coral reef communities, in both cold and warm waters, appear likely as community calcification rates will decrease with decreasing saturation state of CaCO₂. In the case of tropical coral reefs, changes in the balance between calcification and erosion will ultimately result in the degradation of the reef structure and hence spatial heterogeneity, a factor likely to amplify shifts in community composition away from calcifiers towards algal-dominated ecosystems.

Potential shifts in community structure for pelagic open-ocean systems are more elusive. For example, while marine photosynthesis appears to benefit from increased levels of CO₂, the extent of this CO₂ fertilization effect depends on the physiological characteristics of individual phytoplankton groups. Groups with a comparable inefficient carbon acquisition pathway, such as certain coccolithophores, are favoured. Climate change is projected to enhance stratification and to reduce mixed layer depth, which in turn reduces the injection of macronutrients to the euphotic zone, thus creating conditions more favourable for nanophytoplankton, also including coccolithophores. On the other hand, several studies have reported reduced calcification in response to decreasing calcite saturation state for the coccolithophore *Emiliania huxleyi*, which ranks among the main calcifiers in the pelagic realm. From the preceding, it can be concluded that future physico-chemical conditions might favour nanophytoplankton at the expense of diatoms. The case of *E. huxleyi* exemplifies the interplay between climate change and ocean acidification in shaping future pelagic communities. Its outcome is highly uncertain.

The level of confidence that ocean acidification will change the composition of communities is high, mostly due to the robust evidence available for benthic communities. There is a need to collect better information on non-calcifiers in the palaeorecord and to determine the magnitude of the changes in present key ecosystems.

15.2.2.7 Ocean acidification will impact upon food webs and higher trophic levels
The evidence that ocean acidification will have an effect on food webs and higher trophic levels is limited. There is a lot more information on the effects of ocean acidification on organisms at the base than at the top of the food web. The relatively low sensitivity of nektonic, active organisms to ocean acidification is related to their high capacity for acid–base regulation (see Chapter 8). Elevated CO₂ in body fluids could nevertheless reduce their fitness, for example by depressing foraging, growth, and reproduction. For example, ocean acidification was shown to alter the behaviour of larvae of two coral reef fish and dramatically decrease their survival during recruitment to adult populations, potentially decreasing the sustainability of fish populations (Munday et al. 2010).

Possible changes in the lower trophic levels (Section 15.2.2.6), either as shifts between dominant phytoplankton groups or altered food quality (e.g. altered elemental composition of phytoplankton), are likely to spread across the food chain and affect higher organisms that feed on them. For example, pteropods can represent as much as 93% of the total zooplankton biomass in high-latitude regions (Hunt et al. 2008) and are a key food resource for many predators such as herring, salmon, whales, or seabirds. The pteropod *Limacina helicina* can represent as much as 60% of the prey of the juvenile pink salmon in the northern Gulf of Alaska (Armstrong et al. 2005). Due to their key role as a prey, a decline in pteropod populations has the potential to generate significant changes at higher levels of the food web. However, if pteropods show a considerable decrease in abundance, it is certain that the ecological niche they occupy will not remain empty. Whether predators will be able to use the species that will replace pteropods and whether the new species will have a similar nutritional value is completely unknown.

Finally, it is important to note that the direct biological effects of ocean acidification operate at the cellular level but that it is the expression of these effects in populations and ecosystems that are of societal concern. Scaling from physiological data to the levels of populations and ecosystems remains to be done (Section 15.4.6).

15.2.2.8 Ocean acidification will have biogeochemical consequences at the global scale
Ocean acidification interacts with the major ocean biogeochemical cycles by modifying the rates of
key processes (see Chapter 12). The ongoing uptake of atmospheric $\text{CO}_2$ results in a decrease in the buffer capacity of ocean water. As a result, the strength of the ocean sink for $\text{CO}_2$ is going to decrease in the future, a direct positive feedback of ocean acidification to atmospheric $\text{CO}_2$ levels and hence the earth system. This positive feedback may be as large as 30% in the next 100 years for a business-as-usual scenario. The global rate of calcification is likely to decrease in response to increasing atmospheric $\text{CO}_2$. Model studies project a rather modest negative feedback associated with decreasing $\text{CaCO}_3$ production. If the export of particulate organic and inorganic carbon is tightly coupled through ballasting of the organic fraction by $\text{CaCO}_3$, then a decrease in the number of $\text{CaCO}_3$ particles will translate into a shallower remineralization depth for organic carbon, a positive feedback that could compensate the effects of reduced calcification. At timescales of several tens of thousands of years, the marine sedimentary reservoir of carbonates will provide the ultimate buffer against ocean acidification.

There is evidence that phytoplankton groups with an inefficient carbon acquisition pathway may benefit from increased levels of $\text{CO}_2$. However, in order to have an impact on the large-scale carbon cycle and feed back on atmospheric $\text{CO}_2$, enhanced photosynthesis needs to translate into a strengthening of the export of particulate organic carbon to depth. Changes in elemental stoichiometry, such as increasing the C:N ratio with increasing atmospheric $\text{CO}_2$ (see Chapter 6) might enhance future carbon export. The increased delivery of carbon to depth and its remineralization increases oxygen consumption and might result in a significant extension of oxygen minimum zones. Oxygen minimum zones are sites of intense denitrification, a suboxic metabolic pathway yielding $\text{N}_2\text{O}$, a potent greenhouse gas. An increase in the oceanic source of $\text{N}_2\text{O}$ would correspond to a positive feedback on the earth’s radiative balance.

Potential impacts of ocean acidification on the marine nitrogen cycle include enhanced nitrogen fixation and higher rates of water column denitrification. Both combine to reduce the mean residence time of fixed nitrogen in the ocean. However, given that both sources and sinks could be enhanced, it is not possible to make conclusions about the potential generation of imbalances which are required to cause net changes in the ocean’s fixed nitrogen inventory and ultimately changes in the biological pump. Based on the present understanding, the magnitude of the feedbacks to the earth system involving nitrogen fixation and denitrification are unknown. The limited number of studies which have measured changes in the emissions of climate-active trace gases (e.g. dimethyl sulphide, halocarbon gases) to the atmosphere under elevated $\text{CO}_2$ (see Chapter 11) have yielded contrasting results. The effects thus remain poorly known and have not yet been included in coupled climate-marine biogeochemical models.

Overall, it is likely that ocean acidification will have biogeochemical consequences at the global scale but the magnitude is largely unknown and will remain so until the response of organisms and communities is better constrained.

### 15.2.3 Policy and socio-economic aspects

#### 15.2.3.1 There will be socio-economic consequences

As this century progresses ocean acidification has the potential to affect a wide range of marine organisms, food webs, habitats, and ecosystems that supply important goods and services to humankind (see Chapter 14). Goods and services provided by oceans include the provision of food and food products and their significant contribution to global food security, the ocean’s capacity for carbon storage and regulation of gas and climate, and the ability to regulate nutrients on a global scale. Marine habitats and ecosystems also provide leisure, recreation and well-being, and coral reefs, mangroves, and salt marshes protect our coastlines from inundation and erosion.

The provision of fish (including shellfish) is the most obvious service, currently supplying 15% of animal protein for 3 billion people worldwide, and a further 1 billion rely upon fisheries for their primary protein. The chemistry of $\text{CO}_2$ in seawater is such that polar regions, upwelling waters, deep oceans, and estuaries are likely to be affected first, and these are areas of importance for marine-based human food resources. Some organisms, many of which provide food or are key trophic links, will be
affected by ocean acidification. With an increasing world population becoming more reliant upon marine resources for human consumption, and with other pressures, such as pollution, fisheries exploitation, and coastal development, any further stress to these resources through ocean acidification is of concern.

It is difficult to put a monetary value on the wealth of marine ecosystem goods and services because they are not all fully part of commercial markets or as easily quantifiable as economic services or manufacturing output, but a controversial attempt has been made with a total valuation of US$21 trillion yr⁻¹. For this reason marine goods and services do not carry as much weight in policy decisions as economic and manufacturing values. However, global fish production is valued at US$150 billion yr⁻¹ and tropical coral reefs have an estimated value of US$30 billion yr⁻¹ with the potential economic damage of ocean-acidification-induced coral reef loss estimated to be US$500–870 billion in this century. Despite the difficulty in obtaining an overall valuation, if marine systems become impacted the ramifications of loss of marine goods and services for society will be wide ranging. Overall, the socio-economic consequences of ocean acidification are still unknown and hampered by poor knowledge of the impacts at the ecosystem scale.

15.2.3.2 An ocean acidification threshold that must not be exceeded can be defined

One major question asked by policymakers is ‘At what atmospheric CO₂ concentration will ocean acidification have significant, unacceptable, and irredeemable consequences?’. That is, is there a universal tipping point for ocean acidification which should be avoided? Observations performed around CO₂ vents show that a significant decline in biodiversity occurs below a mean pH₅ of 7.8 (Hall-Spencer et al. 2008). It is difficult to use these data to define a critical threshold because the variance of pH around vents is large and the changes in biodiversity may be due to the lower end of the pH range rather than to the mean value.

Some attempts have been made to define global thresholds. The US Environmental Protection Agency quality criteria for water state: ‘For open ocean waters where the depth is substantially greater than the euphotic zone, the pH should not be changed more than 0.2 units outside the range of naturally occurring variation’. According to Schubert et al. (2006), the pH value of near-surface waters should not drop more than 0.2 units below the pre-industrial average value of 8.18 (pH scale not mentioned) in any larger ocean region (nor in the global mean). Rockström et al. (2009) have introduced the concept of planetary boundaries for estimating a safe operating space for humanity with respect to the functioning of the earth system. Ocean acidification is one of the nine boundaries proposed and the proposed control variable is the carbonate ion concentration. As a first estimate, Rockström et al. (2009) proposed a boundary where oceanic aragonite saturation state Ωₐ is maintained at 80% or higher of the average global pre-industrial surface-seawater Ωₐ of 3.44.

The spatial and temporal averaging to which the thresholds refer is often not mentioned, despite the fact that it is critical to do so because pH is subject to strong natural variability. All of these thresholds have been defined without any clear biological, ecological, or biogeochemical foundation. Furthermore, the nature of organismal responses is such that different species will react differently, each having different CO₂ and pH sensitivities which may depend on other factors such as the health of the ecosystem in which they dwell, food availability, and the presence of other stressors such as pollution and warming. Although ocean acidification is a global issue, different regions will be affected at different times (Fig. 15.1) making the definition of a threshold even more difficult.

One hundred members of the global network of science academies, the Interacademy Panel (IAP), signed up to a statement on ocean acidification which stated that ‘even with stabilization of atmospheric CO₂ at 450 ppmv, ocean acidification will have profound impacts on many marine systems. Large and rapid reductions of global CO₂ emissions are needed globally by at least 50% by 2050’. Others have stated that even 450 ppmv is too high, and that atmospheric CO₂ should be stabilized at 350 ppmv to prevent catastrophic decline in coral reefs due to warming and acidification (e.g. Veron et al. 2009).
Although it is critical to provide one or a few acidity level(s) that should not be exceeded, it is a very challenging task which requires a large body of scientific evidence, including at the ecosystem level and on food webs, and the knowledge of the level of risk that society is prepared to accept.

### 15.3 Ecosystems at risk

Three areas of the global ocean are more susceptible to ocean acidification than others, either because ocean acidification will be more severe (polar regions and the deep sea) or because it acts

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**Figure 15.1** Projected regional changes in ocean chemistry likely to be experienced by particularly vulnerable ecosystems and compared with global-scale surface-ocean changes (Turley et al. 2010). The transient simulation of climate and carbonate chemistry was performed with the UVic Earth System Climate Model using observed historical boundary conditions to 2006 and the SRES A2 scenario to 2100 (Eby et al. 2009). For each of the six illustrative high-risk marine ecosystems [Arctic Ocean, Southern Ocean, north-east Pacific margin, intermediate-depth north-east Atlantic (500–1500 m), western equatorial Pacific, eastern equatorial Pacific] we have identified in this paper, the blue-shaded band indicates the annual range in ocean saturation state with respect to aragonite, while the green shaded band indicates the range for calcite saturation. Area-average surface-ocean conditions are calculated for all regions with the exception of the north-east Atlantic where area-average benthic conditions between 380 and 980 m have been used. The thickness of the line indicates the seasonal range, with the threshold of undersaturated environmental conditions marked as a horizontal dashed line. The varying evolution in the magnitude of the seasonal range between different regions is due to the complex interplay between changes in stratification, ocean circulation, and sea-ice extent, and distorted due to the non-linear nature of the saturation scale. The corresponding regions from which the annual ranges are calculated are shown shaded. Global ocean surface averages (bottom) are shown, from left to right: CO₂ partial pressure (pCO₂), pH(SWS), and calcite and aragonite saturation. Figure reproduced from Turley et al. (2010) with permission from Elsevier.
15.3 Synergistically with another major stressor (coral reefs).

15.3.1 Polar seas

High-latitude oceans are cold water bodies which have naturally low carbonate concentrations and are therefore most sensitive to ocean acidification (see Chapter 3). During the 21st century, their surface waters will become chemically corrosive to aragonite, first in the Arctic Ocean and a few years later the Southern Ocean. These severe conditions could prevail over much of the surface Arctic Ocean by the end of the century. Furthermore, the aragonite saturation horizon is shoaling (moving upwards) at a rate of 4 m yr\(^{-1}\) in the Iceland Sea, exposing each year 800 km\(^2\) of seafloor to waters undersaturated with respect to aragonite. Despite the high vulnerability of polar areas to ocean acidification, the biological, ecological, and biogeochemical consequences are not well documented and very few perturbation experiments have been conducted. The first results were obtained on the pteropod (pelagic marine snail) *Limacina helicina* which has an important role in the food chain and the functioning of Arctic and sub-Arctic marine ecosystems. Its aragonitic shell serves as a ballast, enabling large vertical migrations, and as a protection against predators. The gross CaCO\(_3\) precipitation of *L. helicina* decreases logarithmically as a function of decreasing aragonite saturation state, but still occurs, at a low rate, in undersaturated waters (Comeau et al. 2010). However, dissolution of CaCO\(_3\) was not measured in this experiment and the saturation level up to which a positive balance between gross CaCO\(_3\) precipitation and dissolution can be achieved is unknown. The recruitment of the benthic life stages of the spider crab *Hyas araneus* was shown to be affected by ocean warming and acidification (Walther et al. 2010). Knowledge about the response of polar organisms and ecosystems to ocean acidification is still in its infancy and it is critical to gather data on these particularly threatened ecosystems.

15.3.2 Deep-sea environments

The depths of the ocean are generally rich in CO\(_2\) because much of the organic material exported by

the biological pump from the surface is mineralized, releasing CO\(_2\) into waters close to the seabed. These deep CO\(_2\)-rich waters have low pH and a sufficiently low carbonate ion concentration that they are undersaturated with respect to CaCO\(_3\) (see Chapter 3), making it difficult for calcifying organisms to live there. With additional atmospheric CO\(_2\) entering the ocean surface, the horizon that separates saturated from undersaturated waters is shoaling. The global-mean depth of the aragonite saturation horizon is projected to shoal from its pre-industrial level of 1090 m to 280 m in 2100 under the IS92a scenario (see Chapter 3).

These changes in saturation may affect aragonitic cold-water corals. Nearly all of these corals now live in deep waters where \(\Omega_a > 1\), but it is projected that by 2100 under the IS92a scenario 70% of them will be bathed in waters where \(\Omega_a < 1\) (Guinotte et al. 2006). Shell- or skeleton-forming animals that live in deep water but above this horizon can currently calcify but may be amongst the earliest to be affected by ocean acidification (Turley et al. 2007). It is projected that as the saturation horizon moves past them they may no longer be able to calcify. Despite the sensitivity of deep-sea environments to ocean acidification, very few data are available on the biological responses. A recent short-term experiment has shown that the important cold-water coral *Lophelia pertusa* seems to be able to calcify in slightly undersaturated water but its rate of calcification decreases by 50% when kept in high-CO\(_2\) seawater (Maier et al. 2009). While tropical coral reefs are built by a large number of species, cold-water coral communities are constructed by one or two species but provide shelter for many others. It is therefore likely that the combined effect of lower calcification and increased dissolution of pre-existing skeletons will have a negative impact on the biodiversity of cold-water coral communities. Deep-sea organisms other than corals may also be affected by ocean acidification as well as by the future reduction in the oxygen concentration (Brewer and Peltzer 2009).

15.3.3 Coral reefs

Coral reefs are CaCO\(_3\) structures located at or near sea level constructed by scleractinian corals and coralline algae. The skeletons of both types of reef builders are particularly soluble because they are
made of aragonite (corals) or high-magnesian calcite (coralline algae). Coral reefs are distributed in waters with a relatively high aragonite saturation state ($\Omega_a = 3.3$ on average; Kleypas et al. 1999). The tropics and subtropics will see the biggest absolute changes in $\Omega_a$ with a projected drop from 4.2 in the year 1820 to 2.3 in 2100 under the A2 scenario (see Chapter 3). Steinacher et al. (2009) found that under the A2 scenario, waters with $\Omega_a > 3$ will disappear by 2070.

Coral reefs in the eastern tropical Pacific are good indicators of what the future of coral reefs could be. Manzello et al. (2008) observed that cements in intraskeletal pores were almost absent. Consequently, these reefs, which experience naturally high CO$_2$ and low $\Omega_a$ as a result of upwelling, are poorly developed, and are subject to high rates of bioerosion. The abundance of cement appears to be correlated to the seawater aragonite saturation state and inversely related to measured rates of bioerosion.

Corals and coralline algae are probably the organisms that have been investigated the most with respect to ocean acidification (see Chapter 7). Although the dependence of calcification rates on the carbonate chemistry is widespread in coral reef organisms, few seem to be resistant to ocean acidification. Increased dissolution and lower calcification will lead, at some point in time, to a transition from net calcification and CaCO$_3$ accretion to net dissolution and net loss of CaCO$_3$. Additionally, zooxanthellate corals lose their endosymbiotic algae at elevated temperature, leading to coral bleaching and high rates of mortality (e.g. Hoegh-Guldberg 1999). The combination of ocean acidification and warming undoubtedly makes coral reefs the ecosystem most threatened by global environmental change (Hoegh-Guldberg et al. 2007). Several critical issues require better investigation: the mechanism(s) that enable some corals to resist ocean acidification, the interaction between coral bleaching and ocean acidification, and the response of natural communities through long-term perturbation experiments in the field.

15.4 Past limitations and future prospects

Synthesis of our present knowledge about ocean acidification and its consequences (Section 15.2), demonstrates that many uncertainties remain. The present section briefly reviews the main reasons for this relatively poor knowledge and provides suggestions on what can be done to make faster progress in the near future.

15.4.1 Limited workforce and funding

In the 1990s, each year, between 7 and 42 individual authors published on the issue of changes to the carbonate system in seawater and their impacts on marine organisms and ecosystems (Fig. 15.2). A significant number of these papers were looking at the general effects of pH on physiological processes, sometimes at very high levels of acidity; fewer than 25 scientists were involved in investigating the effects of the changes in the carbonate system generated by the uptake of anthropogenic CO$_2$. Ocean acidification was not a topic of great interest to scientists, indeed the term had not even been coined. The number of individual authors increased considerably starting in 2005 and reached over 550 individual authors in 2010. This huge increase in the workforce...
is the result of the increase in the number of national and international projects on ocean acidification and the consequent increase of the rate of publication (see Chapter 1). It now seems that the overall magnitude of the workforce is no longer a major impediment for ocean acidification research. Other difficulties, such as technological and conceptual limitations, hamper progress towards a better understanding of the consequences of ocean acidification. However, some key areas such as work at the community level as well as social and economic science are still limited by the number of scientists involved.

15.4.2 Inappropriate or inconsistent methods

As more and more results on the sensitivity of organisms and communities to ocean acidification become available, the breadth and depth of our understanding of causes and consequences grows. At the same time, the evolving picture becomes blurred by conflicting results. While part of this may simply reflect species-specific differences or the plasticity of organisms in responding to environmental stressors, part of the discrepancy may result from inappropriate methodology, poorly constrained experimental protocols, or misinterpretation of the data. Inconsistencies of this sort may originate from shortcomings such as:

- insufficient control and incomplete description of seawater carbonate chemistry,
- interference through confounding factors, such as temperature, nutrient and oxygen concentrations, irradiance and diurnal cycles,
- lack of acclimation of the test organisms to experimental conditions, causing stress- rather than treatment-related responses,
- pseudoreplication, i.e. the lack of independent, interspersed replicates at the treatment level,
- use of isolates kept in culture over years and decades which may have undergone phenotypic or genetic change unrelated to ocean acidification,
- reporting and interpreting observed responses in relation to mean values, e.g. of pH and $pCO_2$, when in fact large variations in carbonate chemistry occurred during the experiment,
- inappropriate normalization of measured data (e.g. normalizing per cell and per unit biomass may yield very different interpretations if cell size differs between treatments).

These and other possible pitfalls in ocean acidification research are addressed and recommendations for proper experimentation provided in the Guide to best practices for ocean acidification research and data reporting (Riebesell et al. 2010a). It is therefore hoped that future experiments will strictly follow these guidelines, hence helping to avoid confusion in the literature generated by inconsistent methods and data reporting.

15.4.3 Duration of experiments

The current anthropogenic ocean acidification is a very fast process compared with previous episodes in the geological past (Section 15.2.1.3; see also Chapter 2) but still long compared with the generation time of most marine organisms. Adaptation, i.e. adjustment to environmental change by genetic change, is much more likely in microbes than in multicellular marine organisms because they reproduce quickly relative to the timescale of global change and have large populations (Section 15.2.2.5). Their short generation time of a few days allows for thousands of generations by 2100, hence increasing the accumulation of mutations and, at least for prokaryotes, more efficient lateral gene transfer. Perturbation experiments have been the method of choice for investigating the effects of ocean acidification. They were conducted over periods of time (hours to weeks) that may have been long enough to reach a steady-state physiological response but too short to reach a ‘steady-state’ evolutionary response. There is a strong need to carry out longer experiments, encompassing hundreds or thousands of microbial generations. Such experiments have been performed in a green microalga found in soils and freshwater (Collins and Bell 2004, 2006), providing interesting insight for ocean acidification research. First, lines of this alga either increased photosynthesis without increased growth or both their growth and photosynthesis were insensitive to elevated $CO_2$. Specimens found in the vicinity of natural $CO_2$ springs exhibited a similar phenotype,
suggesting that laboratory selection experiments can be used to predict the response of natural populations. Second, the evolutionary response differed in both direction and magnitude from the short-term (physiological) response to elevated CO₂ as it involved an increase in both photosynthesis and growth. The fact that short-term responses may not scale up predictably to longer timescales is worrisome, as current projections of the consequences of ocean acidification are almost exclusively based on short-term experiments. It highlights the need to perform experimental tests of evolutionary responses to elevated CO₂ in marine phytoplankton (Bell and Collins, 2008). Genomics, transcriptomics, proteomics, and assessment of the expression of specific marker genes for crucial functions are promising methods that are or soon will be available to tackle these issues.

15.4.4 Interactions with other stressors

Ocean acidification occurs simultaneously with changes in other environmental variables associated with anthropogenic climate change, including ocean warming, expanding hypoxia, changes in salinity, physical disturbance, mixing, and stratification. There are many examples in the geological record of pronounced extinction events when several environmental stressors were imposed at once (see Chapter 4). Future concurrent changes in some environmental variables may have synergistic effects with ocean acidification, amplifying or dampening the sensitivities of organisms to reduced pH and increased pCO₂. Several of these variables act together in constraining the window for performance of organisms (Pörtner 2010). For instance, as discussed by Pörtner and Farrell (2008), ocean acidification can narrow the thermal window of some animals, thereby further reducing their geographical distribution in a warming ocean. So far ocean acidification research has given little attention to multiple interacting environmental stressors. Future studies should therefore expand to test for synergetic effects of environmental stressors with ocean acidification.

In addition to interference from environmental stressors, the response of an organism to a perturbation such as ocean acidification may also be modified in the presence of competitive or trophic interactions. Hence, results obtained in isolation from other relevant influences need to be verified under more realistic conditions with multiple interacting variables. This calls for an extension of community-level investigations (see also Section 15.4.6). For an integrated assessment of the effects of ocean acidification on marine life it will therefore be crucial to cover the entire range of possible interacting influences and to employ a wide spectrum of approaches from subcellular to ecosystem-level experimentation and modelling.

15.4.5 Lack of field evidence other than around CO₂ vents

The abrupt changes and short duration of perturbation experiments are key limitations (Section 15.4.3) and it is critical that the predictions and projections made using such experiments can be corroborated using field data. Two approaches, observations across natural CO₂ gradients and retrospective studies, have been used with mixed success; just a few examples are provided in this section. The north–south shift from ‘overcalcified’ to weakly ‘calcified’ cells of the coccolithophore *E. huxleyi* in the Southern Ocean reflects a shift in dominance from one ecotype to another, rather than the environmental effect of decreased carbonate ion concentrations and calcite saturation state on a single ‘apparently cosmopolitan’ population (Cubillos et al. 2007). Observations at CO₂ vents (e.g. Hall-Spencer et al. 2008) have demonstrated that ocean acidification does have significant effects on benthic primary producers, calcifiers, and biodiversity. Retrospective studies have provided outcomes that are much less clear, because attribution to a single environmental factor has proven difficult. Grelaud et al. (2009) found an increasing carbonate mass in coccolithophore shells from 1917 to 2004 concomitant with rising pCO₂ and sea-surface temperature in the region of the Santa Barbara Basin, California. Although perturbation experiments suggest that coral calcification may have decreased by about 10% since the beginning of the Industrial Revolution, the evidence for this has not yet been found in field samples. Some (e.g. De’ath et al. 2009), but not all, retrospective studies show decreasing trends in calcification
for the past several decades, but whether the decreases are due to ocean acidification, some other environmental factor (e.g. warming), or a combination of factors remains unclear.

The issue of attribution is a well-known problem in studies of the effects of climate change. Rosenzweig et al. (2008) compiled a huge database and used innovative statistical approaches to demonstrate that changes in physical and biological systems are pervasive and could probably be attributed to climate change caused by increasing concentrations of greenhouse gases. However, this approach is limited by the short time span of many datasets (Zwiers and Hegerl 2008), especially from marine systems, and does not provide the contribution from the major variables such as CO$_2$, temperature, or nutrients.

15.4.6 Limited work at the community level

Progress in our understanding of the possible impacts of ocean acidification on marine life is partly limited by the scarcity of information on responses at the community and ecosystem levels. Results obtained in single-species experiments are not easily extrapolated to natural systems due to the lack of information on the influence of competitive and trophic interactions on single-species responses. To close this gap two approaches are particularly promising: (1) community-level studies in natural high-CO$_2$ environments and (2) CO$_2$ perturbation experiments at the community and ecosystem level. Both approaches have provided important information on the effects of ocean acidification on natural marine communities. The best known example for a natural high-CO$_2$ environment is a CO$_2$ venting site in the Gulf of Naples, Italy, where a community shift was observed along a pCO$_2$ gradient, with calcifying organisms successively disappearing from the community towards the CO$_2$ venting site (Hall-Spencer et al. 2008). Community-level perturbation experiments have been conducted on both pelagic and benthic communities using mesocosm enclosures (Langdon et al. 2010; Riebesell et al. 2010b; Widdicombe et al. 2010). The so-called free ocean CO$_2$ enrichment (FOCE) system uses injection of acid or of CO$_2$-enriched air with controlled-loop pH feedback to maintain a set pH in a small volume (Kirkwood and Sano 2009).

Each of these approaches has strengths and weaknesses. Natural high-CO$_2$ environments capture the full scope of ecosystem interactions over long timescales (at least for the benthos), thereby providing crucial information on the effects on ocean acidification on trophic and competitive interactions and the potential for adaptation. The high spatial and temporal variability in pCO$_2$ and pH, however, makes it difficult to determine a reliable dose–response relationship, complicating the use of this information in projecting the response to future high-CO$_2$ scenarios. The interpretation is also complicated by the uncontrolled advection and recruitment of organisms from unperturbed adjacent areas. The latter problem also applies to FOCE-type experimental systems. Both approaches are restricted to benthic communities with non- or slowly migrating organisms. In contrast, mesocosm enclosure experiments, which range in size between one and a few hundred cubic metres and can be used for both benthic and pelagic communities, have the advantage of well-controlled carbonate chemistry and the absence of exchange with unperturbed surrounding waters. Their limitation lies in the fact that mesocosm experiments generally exclude migratory organisms and their duration is limited as a result of undesirable effects due to the growth of organisms on the walls, which limit their scope with respect to interaction at higher trophic levels and adaptational responses.

With none of the available approaches providing information on the full range of ecosystem responses, progress in our understanding of long-term, ecosystem-level impacts of ocean acidification requires the integration of: (1) community-level experimental studies, (2) field observations in high-CO$_2$ environments, and (3) ecosystem modelling with (4) single-species laboratory experiments addressing the mechanisms underlying the observed sensitivities and (5) long-term high-CO$_2$ exposure experiments examining the potential for adaptation.

15.4.7 Difficulties in performing meta-analysis

Meta-analysis, which statistically combines the results of several studies that address a shared research hypothesis, is a method of choice for
assessing the overall effect of ocean acidification on marine organisms and ecosystems. The recent surge of experimental data has made possible the use of meta-analytical approaches (Hendriks et al. 2010; Kroeker et al. 2010; Liu et al. 2010). Despite their strengths, such approaches have several problems (Borenstein et al. 2009), the most serious of which is the inevitable use of a biased dataset. The ‘file drawer problem’ relates to the fact that studies reporting relatively high treatment effects can be easier to publish whereas those which are inconclusive never get published. This bias may not be extremely serious today as editors may find it exciting to publish data that are inconclusive as they go against earlier conclusions and could raise controversy. It is nevertheless critical that all datasets, inconclusive or not, are published in databases or in data journals (e.g. Earth System Science Data). The other reason for the use of a biased dataset is poor data reporting, which is a serious issue in ocean acidification research. The three recent meta-analyses mentioned above could not use all the data available because many are unavailable or unusable. In their data compilation, Nisumaa et al. (2010) identified 185 papers of interest but data from 85 of them could not be compiled for three reasons: only one parameter of the carbonate system was measured (49 papers), data could not be obtained from the authors (30 papers), or the data were lost (16 papers). The publication of the Guide for best practices on ocean acidification research and data reporting (Riebesell et al. 2010a) will hopefully lead to better data reporting in future publications.

15.4.8 Model development

Present-day state-of-the-art global biogeochemical models mostly rely on the representation of plankton functional types (PFTs). Following this approach, major biogeochemical functions are identified and assigned to specific groups, e.g. CaCO$_3$ production, biogenic silica formation, nitrogen fixation. The growth of each group is directly controlled by the availability of external nutrients. If environmental conditions (light, temperature, nutrients) cross a critical threshold, the plankton functional type disappears from the model world. This approach does not allow for shifts between species within a given PFT, nor for adaptation. This simplistic representation contrasts with the emerging complexity of the biological responses to ocean acidification and challenges the modellers. The evaluation of the impacts of ocean acidification and climate change might well require the development of a new generation of ecosystem models. An alternative to the classical PFT approach consists in the random assignation of physiological traits to a large number of plankton types. This approach makes use of the variability of physiological data reported by experimental studies, rather than identifying a priori a limited number of PFTs which are described by representative mean parameter values. It allows for the emergence of marine communities.

While this approach appears promising when it comes to studying the environmental controls on microbial community structure and ecosystems, its capacity to project the reorganization of communities and ecosystems in response to global warming and ocean acidification remains to be demonstrated.

Future ocean acidification may alter the fitness of organisms, and their differential response is likely to modify the community composition, for example through altered competition between species (Section 15.2.2.6). Optimality-based adaptive models allow one to investigate the synergistic effects of temperature changes and ocean acidification on the basic life functions of organisms (e.g. growth, reproduction, maintenance, but also calcification), as well as intra- and interspecific competition (Irie et al. 2010). Conceptual frameworks such as this are widely used in evolutionary biology and it is anticipated that they will be used increasingly in the context of the effects of ocean acidification and climate change. However, extending similar conceptual approaches to the scale of the global ocean remains a challenge.

15.4.9 Need for a coordinated international effort

The ongoing and planned research projects at the national or international scale cover the field of ocean acidification well and have begun to generate critical data. Those research initiatives are at present uncoordinated, which has several consequences.
Although there is a risk of duplication of research which funding agencies might want to avoid during a dire economic situation, it has been minimized among some European projects (EPOCA, BIOACID, and UKOA) thanks to tight integration. A reasonable level of duplication is useful anyway because the replicability of results increases the level of confidence. There are also many activities that would be performed better and more efficiently at the international level. The SOLAS-IMBER Working Group on Ocean Acidification has outlined several priority areas for action: including biological variables in observing networks, launch of joint platforms and facilities, intercomparison exercises, the update of the Guide to best practices for ocean acidification research and data reporting, management of ocean acidification data, training, and outreach. However, there are currently no human resources and very limited funding to support such activities at the international level. The community may need to make a large effort in order to raise support for an international coordination office.

15.5 Conclusions
Some effects of the uptake of anthropogenic CO₂ by the oceans, such as the changes in the carbonate chemistry, are known with a high degree of certainty (Table 15.1). Most biological and ecological effects are much less certain. Nevertheless, there is no doubt that calcification, primary production and nitrogen fixation, and biodiversity will be altered but by a magnitude that is unknown. These changes will in turn generate changes in the biogeochemical cycles, society, and the economy. Whether these changes will be significant or not is also unknown. The levels of confidence for these changes, estimated for the first time in Table 15.1, can be evaluated either with a pessimistic or with an optimistic view. It is unfortunate that so much uncertainty remains, because human society needs to get information with a relatively high degree of confidence before it decides to regulate its activities. Even with a high degree of certainty on future climate change and its likely impacts on society and economy, the reduction of CO₂ emissions is proving extremely slow and difficult to implement. Ocean acidification and its impacts on marine ecosystems may well provide an additional reason for reducing CO₂ emissions but the knowledge generated until now is patchy (many processes and functional groups have not been investigated) and sometimes uncertain and conflicting, making it difficult for policymakers to put ocean acidification high on the agenda.

There is a much more optimistic reading of the levels of certainty summarized in Table 15.1. Although it has been known for a relatively long time that ocean pH will decrease due to the uptake of CO₂, it is only very recently that the biological consequences have been identified. Considering the small number of scientists engaged in ocean acidification research during most of the last 20 years, the level of knowledge reached in less than 20 years is remarkable and compares very favourably with the development of research on the impact of climate change on terrestrial ecosystems. A considerable improvement in the levels of uncertainty can be expected in the coming years due to the recent launch of major national and international projects on ocean acidification, the build-up of a strong community of researchers, and ongoing synthesis efforts of the IPCC. There is no doubt that the near future will be exciting for ocean acidification research. Whether the outcome will confirm the pessimistic view of some scientists in the field or not, it is hoped that human society will consider ocean acidification together with climate change to decide on the best course for its future.

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References


