Paleo-perspectives on ocean acidification

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The anthropogenic rise in atmospheric CO_2 is driving fundamental and unprecedented changes in the chemistry of the oceans. This has led to changes in the physiology of a wide variety of marine organisms and, consequently, the ecology of the ocean. This review explores recent advances in our understanding of ocean acidification with a particular emphasis on past changes to ocean chemistry and what they can tell us about present and future changes. We argue that ocean conditions are already more extreme than those experienced by marine organisms and ecosystems for millions of years, emphasising the urgent need to adopt policies that drastically reduce CO_2 emissions.

Ocean acidification: the 'evil twin' of global warming

One of the major environmental challenges facing society is the impact of increased levels of atmospheric CO_2 and other greenhouse gases on the physical and biological systems on earth. These increased levels are mainly due to the combustion of fossil fuels and changes in land use and deforestation. So far, most research has focused on the impacts arising from global warming which has driven (and is continuing to drive) large fundamental changes in biological systems. However, the steady acidification of the oceans (nicknamed the 'evil twin' of global warming) is another insidious consequence of rising levels of atmospheric CO_2. Although it will be hard to quantify the effects separately, and indeed their synergistic behaviour, evidence gathered over the last years suggests that ocean acidification could represent an equal (or perhaps even greater) threat to the biology of our planet.

A large proportion of the CO_2 emitted by the activities of humans is taken up by the oceans. This uptake accounts for ∼50% of the CO_2 released from the combustion of fossil fuels and cement production, or 30% if land-use practices such as deforestation are also included [1]. As CO_2 dissolves in the oceans, it takes part in a series of reactions leading to a drop in pH (Box 1). This change in seawater chemistry affects marine organisms and ecosystems in several ways (Boxes 2 and 3), with the clearest impacts being felt by organisms that produce shells and skeletons composed of calcium carbonate. Due to the CO_2-induced decrease in concentration of carbonate ions in seawater, the saturation state of the

precipitated calcium carbonate decreases progressively as pH decreases, making calcification more difficult (Box 1). In addition, ocean acidification can also disrupt pH-sensitive physiological processes such as gas exchange and reproduction ([2] and references therein). Reduced pH will also alter the chemistry of nutrients and the chemical form of metals in seawater, which might enhance their role as micronutrients (e.g. iron) or their toxic potential (e.g. copper and zinc). On a broader scale, changes to the physiology of keystone organisms such as pteropods, coccolithophorids, foraminifera and corals could lead to vast changes to fundamentally important ecosystems and/or food webs, with consequences for the carbon cycle and the exchange of gases between the ocean and the atmosphere [2–8].

The surface waters of the oceans have already acidified by an average of 0.1 pH units from pre-industrial levels [2], with future changes depending ultimately on the rate at which CO_2 is emitted by the activities of humans. Surface-water pH reductions could range from 0.2 units if 1,200 GT C (1 GT = 10^{15} g) are released over 1000 years to nearly 0.8 units if 5,000 GT C are released over 200 years [9]. By the end of the twenty-first century, projections based on different scenarios indicate that ocean pH will have decreased by 0.3 to 0.4 pH units ([10], Box 1). As this review will show, current conditions are probably more extreme than those experienced by the oceans over a timescale of millions of years, and future conditions will certainly be more extreme. However, an important degree of spatial (Box 4) and temporal (Figure 1) heterogeneity exists in seawater pH, and the decreasing trend in ocean pH will be more pronounced in some areas than in others. Higher latitudes, for instance, will experience the greatest change, whereas the tropics will apparently experience less change [10]. Consequently, conditions are likely to become very hostile for calcifying species in the northern high latitude regions over the next decade [10] and in the Southern Ocean over the next few decades [11,12]. This does not, however, militate against large-scale changes which are occurring (and will continue to occur) in tropical regions [3–6].

Understanding the implications of these changes in seawater chemistry for marine organisms and ecosystems is in its infancy. However, interest in this issue has deepened in the past five years, with a growing number of researchers investigating the widespread implications and potentially catastrophic consequences of ocean

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Box 1. Basics of chemistry changes in seawater from the marine absorption of CO_2.

As CO_2 dissolves in seawater, it participates in a series of chemical equilibrium reactions ((1) in Figure Ia) which result in increased concentrations of bicarbonate and hydrogen ions (protons) and therefore a decrease in seawater pH (Figure Ib). This also leads to a decrease in the concentration of carbonate ions (Figure Ib), with implications for marine organisms that need them as building blocks in the construction of their calcium carbonate skeletons or shells. For most of these organisms, experimental studies have demonstrated that this change in seawater chemistry makes calcification more difficult (Boxes 2 and 3).

Marine organisms can precipitate calcium carbonate in the form of calcite (e.g. coccolithophorids, foraminifera), aragonite (e.g. corals, pteropods), or high-magnesium calcite (e.g. crustose coralline algae). These crystal structures have different degrees of stability. Calcite is thermodynamically the most stable, followed by aragonite and finally by high-magnesium calcite, which is the least stable. The tendency for a structure to dissolve is strongly influenced by the saturation state (Ω) of each particular mineral phase, which is related to the concentration of calcium and carbonate ions in the seawater (equation (2) in Figure Ia). Over geologically short timescales (<1 million years), the concentration of calcium ions in seawater does not vary considerably, so a decrease in carbonate ion concentration due to ocean acidification will reduce Ω. Precipitation of calcium carbonate is thermodynamically favourable where $\Omega > 1$ (super-saturation) and unfavourable where $\Omega < 1$ (under-saturation). However, the Ω threshold for biogenic precipitation depends on each marine species. Coral reef communities and structures, for example, develop properly in seawaters where Ω values of aragonite are >3.3 [5,83] because the calcification process has to exceed rates of bio-erosion.

As oceans turn more acidic, the saturation state of aragonite progressively decreases, reducing the effective area where coral reefs can develop (Figure Ic). Evidence for these declining trends in Ω has recently been reported from the Caribbean [85]. The chemical reaction (3) in Figure Ia is one of the ways to represent the precipitation of calcium carbonate, and illustrates the counter-intuitive fact that, when marine organisms calcify, there is a release of CO_2 in the surrounding water. However, the amount of CO_2 released per mol of calcium carbonate precipitated depends on a range of factors including temperature, salinity and pCO_2 [86]; in today's oceans, the CO_2 released per mol of calcium carbonate precipitated is of ~0.6 mol, but this figure will increase as the atmospheric concentration of CO_2 rises.

Figure I. Chemistry of ocean acidification and global changes in aragonite saturation. **(a)** Schematic view of the anthropogenic perturbation of the carbon cycle in which part of the CO_2 emitted from the combustion of fossil fuels and deforestation is absorbed by the oceans. (1) Chemical equilibrium reactions in which CO_2 intervenes as it dissolves in seawater, where K_1 and K_2 are the dissociation constants for carbonic acid and bicarbonate ion, respectively. (2) Definition of the saturation state (Ω), where K_{sp} is the solubility constant of each mineral phase. (3) Calcium carbonate precipitation reaction that illustrates the release of CO_2 as precipitation occurs. **(b)** Near past (1800) and near future (2100) evolution of surface pH (orange, on total scale) and atmospheric CO_2 (magenta) from [10] based on prescribed fossil- fuel and land- use CO_2 emissions from historical data for the period 1820 to 2000 and considering the A2 IPCC SRES emissions scenario afterwards. Evolution of bicarbonate (green) and carbonate ion (blue) concentrations, computed from dissolved inorganic carbon and pH data from [10]. These calculations were done using the CO2SYS.XLS program (Pelletier *et al.*, available at www.ecy.wa.gov/programs/eap/models.html). The grey cloud of points shows all 1×1 degree mixed surface layer (upper 50 m) pH values in the oceans, computed from total carbon and alkalinity data (see Box 4 for more details). **(c)** Reconstructions for the past and present, and predictions for the future changes in the aragonite saturation state (Ω, equation (2) in Figure Ia) at different levels of atmospheric CO_2 concentrations (white numbers in ppmv; reprinted with permission from [5]). Note the dramatic reduction in blue areas, which are representative of the approximate minimum $\Omega_{aragonite}$ values needed for carbonate coral reef communities to develop properly [83].
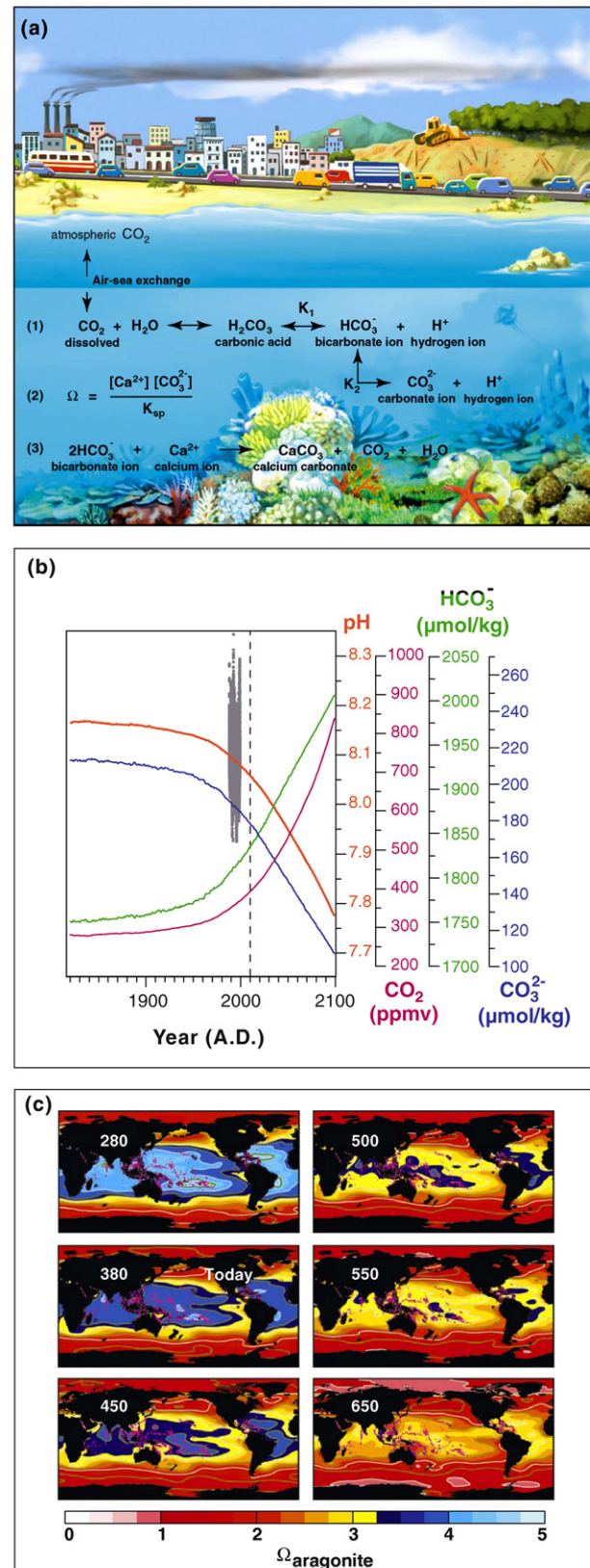
Box 2. Brief account of contemporary biological impacts of ocean acidification

Photosynthesis and primary production

CO_2 and reduced pH have relatively minor effects on the photosynthesis of marine plants [2] due to the presence of carbon- concentrating mechanisms that control the influence of pH and flux of CO_2 into the photosynthetic organisms [87]. Exceptions occur in the case of calcareous phytoplankton, which may sometimes benefit from the rise of atmospheric CO_2 [71,88]. At the community level, some data also suggest increased carbon fixation under high CO_2 conditions [89,90]. Changes in the speciation of nutrients with the lowering of pH (e.g. a shift from ammonia to ammonium or a decrease in phosphate) might also affect phytoplankton productivity.

Calcification

Calcification of marine organisms appears to be highly sensitive to the concentration of carbonate ions. Doubling the partial pressure of CO_2 above seawater leads to a decrease in calcification of 9–29% and 4–8% for coccolithophores and foraminifera, respectively [7], and of 9–59% for reef-building corals [3,4,7]. These changes may 'tip the carbonate balance' of ecosystems such as coral reefs into the negative, given the large amount of calcium carbonate that is taken away by natural processes associated with physical and biological erosion (see Box 3). Crustose coralline algae show similar responses, with decreases in calcification that are exacerbated at higher temperatures [91,92]. Regarding coccolithophores, there appears to be considerable variability between species (e.g. [93]) and even within single species ([94] and references therein). Interestingly, Langer *et al* [94] recently reported very different responses of calcification to acidification in different strains of the coccolithophore *Emiliania huxleyi*, suggesting a genetic basis for their origin.

Information on the effects of elevated pCO_2 on the calcification of other organisms has grown sharply over the past five years. For example, shelled pteropods, which are an important component of high- latitudes seas ([6] and references therein), are sensitive to elevated pCO_2 [6,11,95]. Shell growth has decreased in gastropod and bivalve molluscs under lowered-pH conditions [96,97]). Similarly, elevated pCO_2 is also likely to impact calcified organisms such as echinoderms [98] and crustaceans [99], although in complex ways. Impacts that result from reduced skeletal mass and thickness are likely to influence predation and competition, although these impacts have yet to be demonstrated. Recently, a mixture of responses of marine calcifiers to ocean acidification has been seen in a study encompassing multiple species [100].

Reproduction

Most marine organisms have larval stages which spend anywhere from days to months as plankton before settling into benthic populations. The larval stages are particularly sensitive to changes in the chemical and physical environment, and several studies have documented the impacts of ocean acidification on this important life- history stage. Impacts range from decreased fertilisation as a result of reduced pH to the disruption of larval shells and skeletal structures (see review in [99]). Impacts also include reduced hatching success, larval growth and settlement across a range of organisms including reef- building corals, molluscs, echinoderms, copepods and krill. Other studies have documented the reduced larval settlement and recruitment of important organisms such as crustose coralline algae [101] and corals [102].

Impacts on other physiological processes

Increased pCO_2 can have direct effects on the pH and buffering capacity of cells and tissues, affecting processes such as ion transport, enzyme activity and protein structure. It can also have a big impact on the delivery of oxygen to tissues, most importantly affecting species with high metabolic rates. Metabolic suppression might arise under reduced pH and elevated pCO_2, and is considered to be an adaptive response for surviving short- term hypercapnia and hypoxia (e.g. [103]). In these cases, acidosis of the tissues leads to decreased energy use, as well as reduced protein synthesis and respiratory activity (e.g. [103,104]).

acidification. Here, we summarise recent discoveries published over the last 4–5 years placing particular emphasis on what we can learn from past conditions experienced by the oceans. We also explore the growing body of information from field studies which verify projections arising from experimental and modelling studies. In doing so, our review paints an urgent picture of a rapidly changing ocean and further emphasizes the conclusion that the current CO_2 emission pathway is unsustainable and will have costly consequences for ocean ecosystems.

Evidence of ocean acidification from instrumental time series

The instrumental measurement of pH in seawater has challenged scientists for decades [13]. Recent advances in indicator-based spectrophotometric techniques have allowed the detection of changes in pH arising from the anthropogenic release of CO_2 [13], with a few time-series now of sufficient length and quality to record reductions in ocean pH. Examples are those of the North Atlantic Ocean near the Bermuda Islands [14], the subtropical North Pacific Ocean near Hawaii [15], and the northeast Atlantic subtropical gyre close to the Canary Islands [16,17]. Superimposed onto characteristic annual cycles, all of these series show a clear decreasing trend in ocean pH of ~0.017 to 0.020 pH units per decade (Figure 1a), with pH decline proceeding more rapidly at higher latitudes [18,19].

Temporal variability exists in seawater pH, often in the form of cyclic oscillations of various amplitudes and periodicities. Several physical variables and biological processes drive this variability in pH, including temperature, salinity, upwelling, water currents, river runoff, sea ice melt, photosynthesis, respiration, calcification and dissolution. This variability is often more extreme in coastal areas. Two examples of daily variability in pH in very shallow coastal areas are shown in Figure 1b [20,21]. This variability is typical of coastal environments dominated by calcareous organisms and is of significantly higher amplitude than the characteristic annual pH cycles of the open ocean. This is despite the fact that the development of phytoplankton blooms in the open ocean often amplifies the variability of the CO_2 system chemistry for short periods of time [22]. Seawater pH in particular coastal areas is also heavily influenced by riverine inputs [23,24] and by the upwelling of cold and low-pH seawater, a natural phenomenon with biological impacts that are being exacerbated by the marine absorption of anthropogenic CO_2 [25]. Like its evil twin, global warming, ocean acidification will be superimposed on the natural (daily, seasonal, inter-annual) variability of the ocean carbonate system, resulting in new extremes and ranges of oceanic pH.

The paleontological context of current and future changes

Current instrumental records of oceanic pH cover only a few decades. However, it is important to go further back in time if we are to fully understand ocean acidification and its impacts. This is essential to understand the context of the changes that we are facing; to unravel impacts and responses of marine biota to previous changes in pH; to test

## Box 3. Ecological consequences, with insight on coral reef ecosystems

The relative differences in sensitivity to ocean acidification within groups of organisms are likely to lead to changes in community structure, with some species doing better than others over time. Equally, changes in the abundance of particular species will drive the abundance of other species that could prey on them or use them as habitat. The distribution of species could also change as the carbonate saturation horizon shallows and contracts to lower latitudes. For example, pteropods might shift to lower latitudes as the saturation state of surface waters at higher latitudes approaches under-saturation. Many of the ecological consequences of ocean acidification have yet to be reported, but the specific example of coral reefs illustrates several issues that are likely to arise as the calcification of benthic communities of corals and crustose coralline algae declines.

Carbonate coral reefs are the most biologically diverse marine ecosystem on the planet, occupying shallow-water, sunlit habitats where the aragonite saturation state (Box 1) is >3.3 [5,83]. Under these conditions, dense communities of reef-building corals develop, making extensive aragonite skeletons which build- up over time to produce the framework of coral reefs. Other marine calcifiers such as red calcareous macroalgae (e.g. *Porolithon*) grow over the solid remains of dead corals, 'gluing' together dead coral skeletons and leading to the development of the reef framework. The calcareous skeletons of other organisms such as green calcareous macroalgae (e.g. *Halimeda*), invertebrates and foraminifera contribute to the production of calcium carbonate in the coral reef, which ultimately balances physical (e.g. waves, storms) and biological erosion (e.g. excavating cyanobacteria, plants and animals). Under conditions where calcification can keep up with or slightly exceed the rate of erosion, carbonate coral reefs prosper.

However, reef- building corals are sensitive to ocean acidification [4,5], with calcification rates falling sharply as carbonate ion concentrations decrease. Given that the rate of erosion is often ≥90% of the rate of calcification (e.g. [105] and references therein), small changes in the calcification rates can put coral reefs into a negative carbonate balance. Under these conditions, coral reefs no longer grow and, in many circumstances, begin to crumble and disappear. These issues are exacerbated by the high degree of sensitivity of reef- building corals to the synergistic effects of increased sea temperatures [91] which further decreases calcification and survivorship of coral polyps. Taken together, most of the evidence suggests that carbonate coral reefs are likely to disappear as atmospheric CO_2 approaches 450 ppmv and average global temperatures rise to 2 °C above the pre-industrial period [5,77] (Figure I). Recent evidence suggests that these changes are already occurring, with the observation that coral cover on tropical reef systems is 30–50% lower than that seen on the same coral reefs in the early 1980s [106].

The loss of calcifiers from the world's carbonate coral reef systems has several serious ecological consequences. First, these changes will lead to a loss of tens of thousands of species which use coral reefs as habitat [107–110]. Second, the loss of coastal protection provided by coral reefs will lead to increased wave-stress on sensitive habitats such as seagrass and mangrove communities. This is likely to lead to major changes in coastal processes. Third, the dwindling productivity of coral reefs will have knock-on effects on fisheries and other benefits that currently support >500 million people worldwide [5].
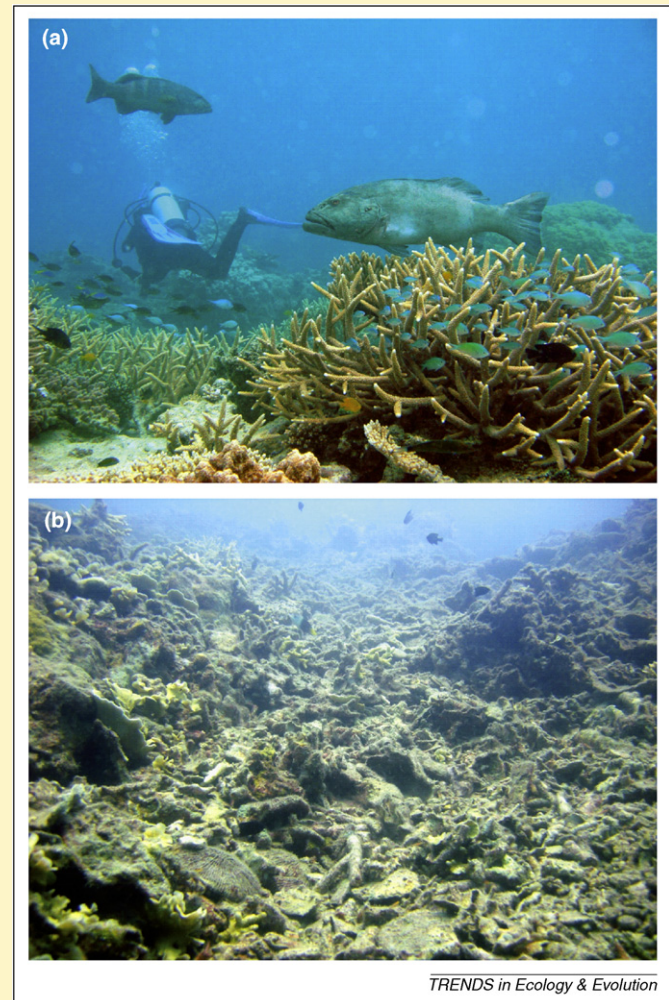
Figure I. Coral reef ecosystems are facing enormous challenges in the face of global warming and ocean acidification. **(a)**. Coral dominated ecosystem from the southern Great Barrier Reef. **(b)**. Coral reef from Karimunjawa, Indonesia, illustrating the impacts of losing reef calcifiers as a result of poor water quality and physical damage. The latter is analogous to the condition expected if coral reefs continue to experience the warming and acidification of oceans. [Photos by O. Hoegh-Guldberg].

and validate, under past conditions, the physical and bio-geochemical models that are used for making future projections; and to investigate if the marine biota is already being affected in the field. For this reason, paleo-reconstructions that use proxies of seawater pH or other related parameters are particularly important. Recent advances in these techniques have begun to illuminate natural cycles and variability over hundreds- to- millions of years.

Proxies of seawater pH and other parameters of the CO_2 system

The CO_2 system in seawater is defined by a series of parameters such as pH, partial pressure of CO_2 (pCO_2), alkalinity and the concentration of carbonate ions ($[CO_3^{-2}]$). The entire system can be determined by knowing the value of any two of these parameters, together with temperature and salinity [26]. Over the past decade, substantial progress has been made in developing reliable proxies for reconstructing how these parameters have varied in the past. As a result, there are now tools for reconstructing seawater pH (e.g. through the analysis of boron isotopes ($\delta^{11}B$) in biogenic carbonates), pCO_2 (from carbon isotopes of marine molecular biomarkers or carbonate in pedogenic minerals, or from stomatal density in leafs) and $[CO_3^{-2}]$ (from foraminiferal shell weights and B/Ca ratios in foraminifera) [27–29].

The $\delta^{11}B$ paleo-pH-meter is beginning to provide valuable, quantitative estimates of past seawater pH over several time-scales [29]. The method in this case relies on the fact that, when calcifying organisms incorporate

Box 4. Spatial heterogeneity in seawater pH

Natural gradients in seawater pH, driven largely by sea temperature, exist in the oceans. These gradients are related to physical and biological processes. Typical horizontal gradients are shown in the surface water pH map of Figure Ia. This map reflects the lowering of pH in areas under the influence of upwelling, where cold deep waters, rich in dissolved inorganic carbon and low in pH, are advected to the surface. This occurs, for example, in the Eastern Equatorial Pacific, the Arabian Sea along the Somalia and Oman coasts, and off the west coast of Africa. For regions not affected by upwelling, the areas where biological production is highest tend to be characterised by the highest values of pH. In these regions, the fixation of dissolved inorganic carbon by phytoplankton and its subsequent transport to deeper layers (by the so-called 'biological pump'), raises surface water pH. In the water column, seawater tends towards lower pH with depth, as illustrated in Figure Ib. This is also a result of the downward flux of carbon fixed in the euphotic zone by phytoplankton, which is remineralized in deeper layers. Interest-

ingly, deep waters of the Pacific Ocean have a significantly lower pH than those of the Atlantic Ocean. This reflects the interactive role of biological activity and the global water circulation of the oceans. Deep waters of the Pacific Ocean have had more time to accumulate CO_2 from remineralization of organic matter than the Atlantic water, owing to their older age (or longer elapsed time since their last contact with the atmosphere as water circulates along the deep conveyor belt from the Atlantic to the Indian and Pacific Ocean). Note also the progressive narrowing of the pH variability range with depth in the three basins, which depicts a significantly more constrained environment in terms of carbonate chemistry at depths below ~3000m. This situation might have led to a minor degree of tolerance to pH changes for species living at these depths compared with those inhabiting shallower water masses. The narrow tolerance limit of benthic species might make them particularly susceptible to future changes in marine chemistry due to ocean acidification ([60] and references therein).
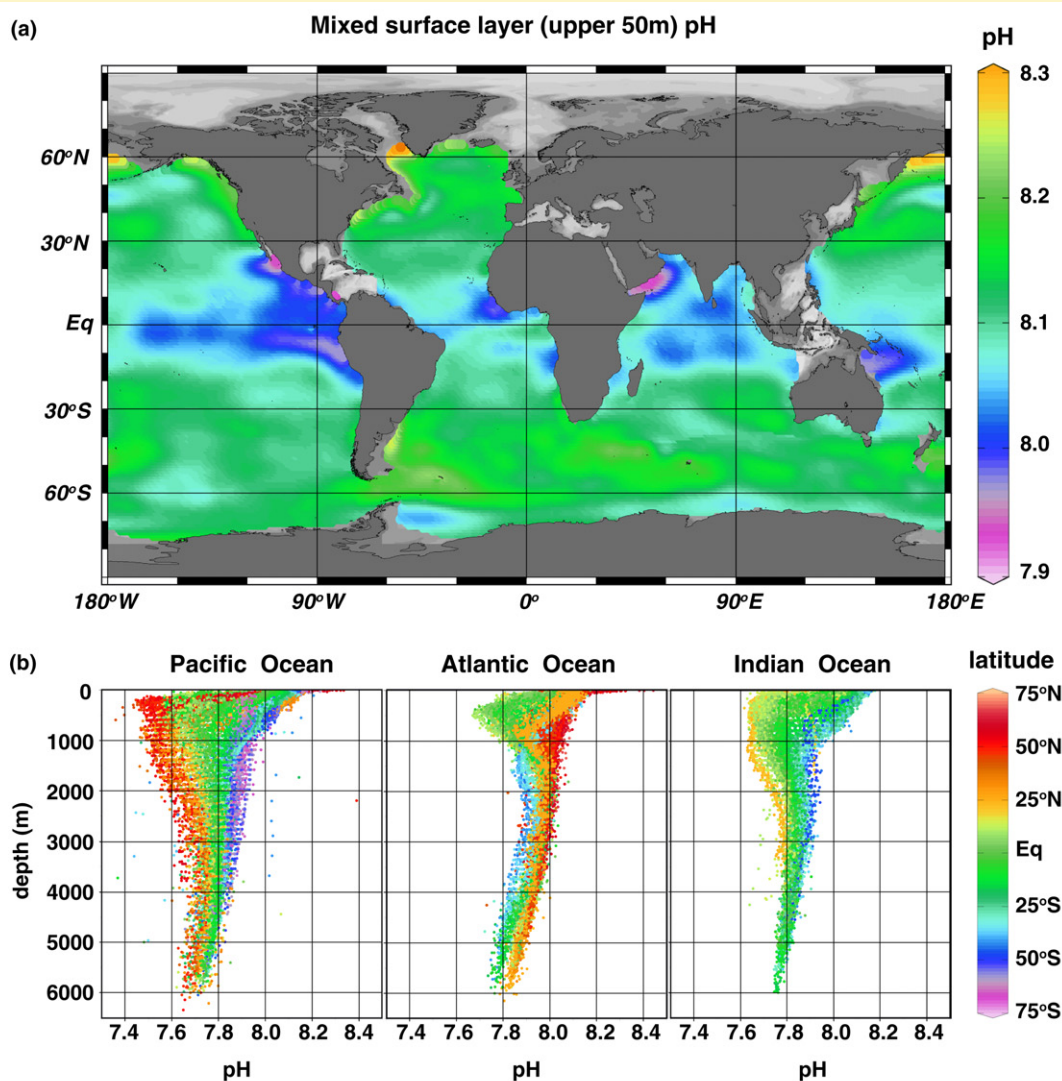
Figure I. Horizontal and vertical variability of seawater pH. **(a)** Map of mixed surface layer (upper 50 m) pH values in the oceans (*in situ*, on the total scale), computed from total carbon and alkalinity data from the GLODAP gridded dataset [84] and annual mean data for temperature, salinity, phosphate and silicate from the World Ocean Atlas 2005 dataset (http://www.nodc.noaa.gov/OC5/WOA05/pr_woa05.html). pH data were computed by means of the CO2SYS.XLS program (Pelletier *et al.*, available at www.ecy.wa.gov/programs/eap/models.html). **(b)** Depth profiles of *in-situ* pH (on the total scale) for the Pacific, Atlantic and Indian Oceans, using colours to highlight differences related to latitude. pH data were computed from the GLODAP bottle dataset [84], using the Schlitzer, R., Ocean Data View (ODV) package (Version 4.0.1; http://odv.awi.de), which includes a built in tool for pH calculation. The three surface profiles and the surface map were plotted with ODV.
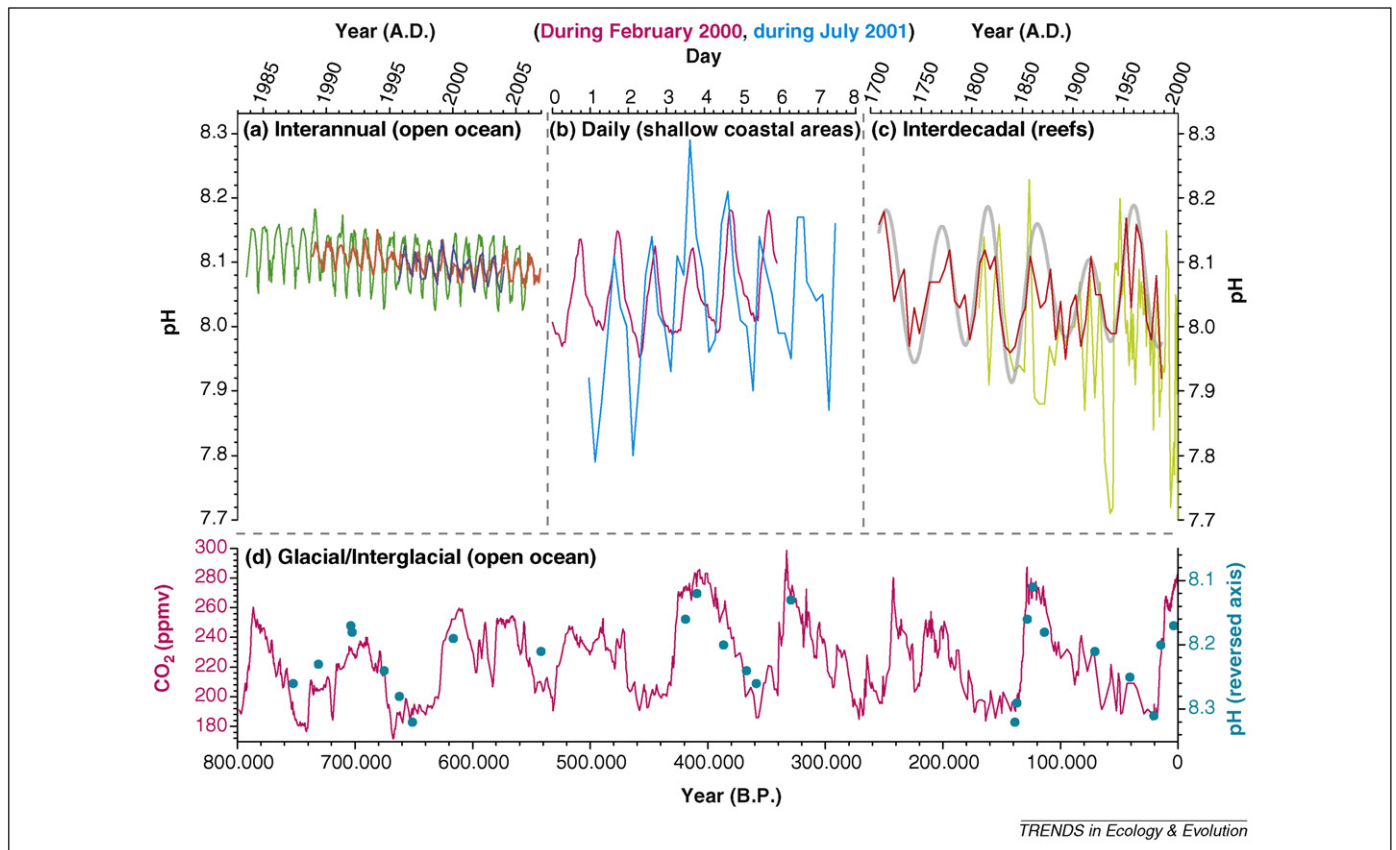
Figure 1. Examples of variability in pH over different timescales. **(a)** Time-series of pH variability at inter-annual scales, measured directly or derived from other parameters of the CO_2 system, in the North Atlantic Ocean near Bermuda (green curve, composite of Hydrostation S and BATS station, [14]), in the subtropical North Pacific Ocean (orange curve, ALOHA station [15]) and in the northeast Atlantic subtropical gyre (blue curve, ESTOC station [16,17]). **(b)** Instrumentally measured daily pH variability in reefs and very shallow coastal areas; Anse des Cuivres, NW Mediterranean Sea (pink curve, data measured during February 2000 [20]) and Molokai Reef flat (cyan curve, data measured during July 2001 [21]). **(c)** Inter-decadal variability in coral reef-water pH from boron isotopes in corals from Flinders Reef, western Coral Sea (red curve, [33]) and Arlington Reef, in the Great Barrier Reef (green-yellow curve, [35]; note that one reconstructed pH value of 7.58 units, on the total scale, for year 1998, was not included due to a possible bleaching influence in the boron isotopic composition of the coral, and that the most recent pH value, for year 2004, would fall slightly out of scale in this plot (pH of 7.67 units)). The grey thick sinusoidal curve overlying the records corresponds to a Gaussian filtering of the Flinders Reef pH record at a frequency of 0.02 ± 0.01 year^{-1}, which highlights the encountered cyclicity of ∼ 50 years [33]. **(d)** Glacial–interglacial variability in surface water pH, reconstructed from boron isotopes in foraminifera (filled blue symbols, [40], note the reversed axis), superimposed on the record of atmospheric CO_2 concentration during the last 800,000 years inferred from the composition of air bubbles trapped in Antarctic ice cores (magenta curve, [36] and references therein, concentrations in ppmv). All pH values correspond to the total scale and have been recalculated accordingly when original data were reported on a different scale.

boron in their structures, they incorporate the borate species, which has a boron isotopic composition that is dependent upon seawater pH. Several calibrations using cultures of different organisms demonstrate reliable pH measurement albeit with small offsets that can be corrected for. Calibrations with *Porites* corals, in particular, showed an excellent match with theoretical predictions [30]. Several analytical techniques have been developed over the last decade for the challenging measurement of $\delta^{11}B$, and the results of an inter-calibration exercise have recently been released [31]. Depending on each technique, $\delta^{11}B$ measurements can be obtained in precisions up to 0.25‰, which would translate into precisions of up to 0.03 pH units.

The use of $\delta^{11}B$ could be more problematic for deep time, beyond 10 to 20 million years, which is the estimated residence time of boron in seawater. Over these timescales, the $\delta^{11}B$ of seawater cannot be considered constant, and needs to be modelled or estimated from other variables (e.g. [32]). Additionally, reconstructions using marine organisms that are no longer extant would require cross-calibration with the isotopic composition of modern

species. With these considerations, however, extending the use of these techniques to deeper time periods should be possible.

Variability from seasons to decades
Analyses of boron isotopes in long-lived *Porites* corals, a genus that has been calibrated for the $\delta^{11}B$ *vs* pH relationship [30], have provided evidence of natural cycles of relatively large amplitudes in seawater over the last three centuries (Figure 1c). For example, intra- and inter-annual cycles of 0.15 to 0.3 pH units were observed at Flinders Reef in the Coral Sea, Australia, probably related to the flushing efficiency of waters over the reef [33]. During periods of poor flushing of reef waters, the build-up of CO_2 due to ecosystem calcification and respiration would lower seawater pH whereas, during periods of rapid renewal of reef waters due to enhanced strength of marine currents, seawater pH would rise to match values typical of the open ocean. These large fluctuations in pH fall within the typical ranges of modern coral reef ecosystems, which exhibit shifts in the CO_2 seawater chemistry of considerably larger amplitude than in the open ocean (Figure 1b)
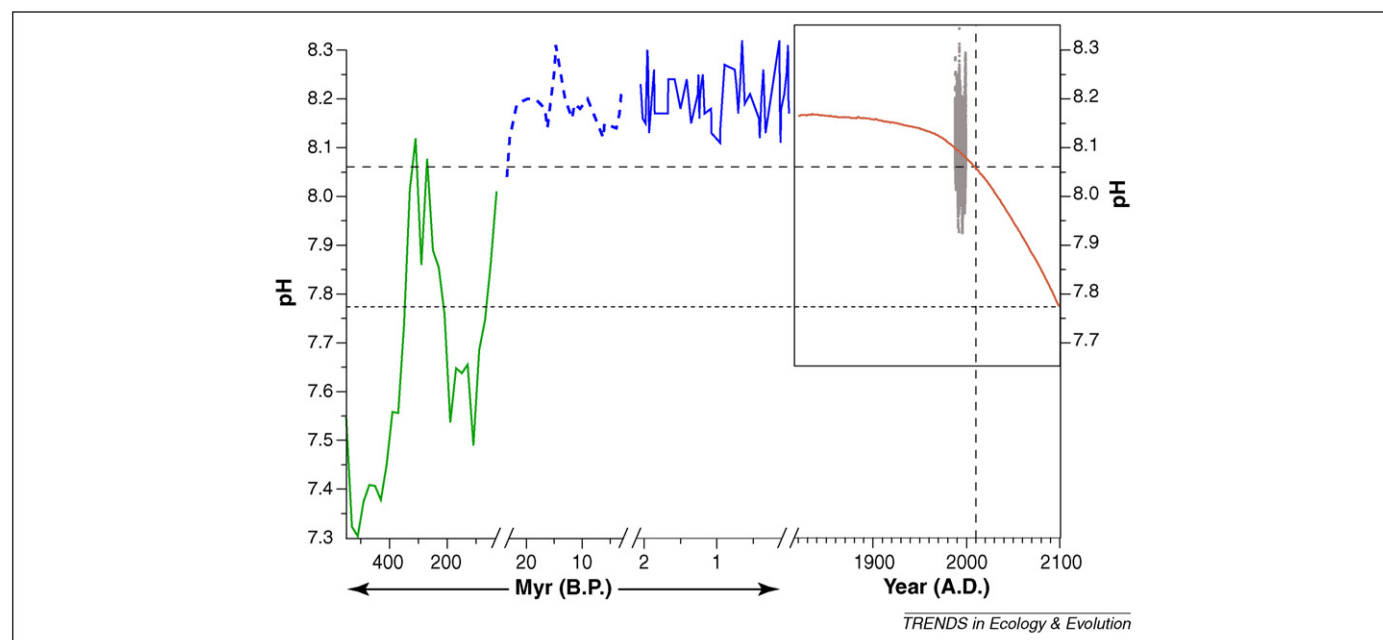
Figure 2. Past, present and future pH trends. The temporal composite of paleo-pH includes data from the output of an atmosphere–ocean–sediment carbon cycling model for the period between 550 Ma and 30 Ma (green curve; [49]), and from two paleo-reconstructions from boron isotopes in foraminifera (dashed blue curve, data from [32] for the period between 23 Ma and 3 Ma and solid blue line, from [40] for the last 2.1 Ma). The inset shows data of surface pH (orange curve) and the grey cloud of points shows all 1 × 1 degree mixed surface layer (upper 50 m) pH values in the oceans, computed from total carbon and alkalinity data (see Box 4 for more details). All pH data are on the total scale. Data from [40] were converted from the seawater to the total scale by the constant addition of 0.01 pH units, which is the average difference between the two scales.

[34]. The Flinders reef reconstruction provides insight into the natural pH ranges in which corals live, and is therefore an important context for predicting the effects of future acidification on marine ecosystems. It highlights the importance of natural variability in reef-water pH, which could potentially enhance or mitigate the vulnerability of corals to future ocean acidification.

A similar pH reconstruction in Arlington Reef, a more coastal reef in Australia, has recently provided further evidence of significant, inter-annual variability [35], with perhaps a signature of the recent anthropogenic ocean acidification over the last decades (Figure 1c).

For further refinement of the coral $\delta^{11}B$ paleo-pH-meter, it would be valuable to compare results from multiple coral cores in the same reef, or calibrate them in areas where reliable instrumental seawater pH time-series exist.

Glacial–interglacial cycles (last ∼2 million years)
A major achievement of paleo-reconstructions is the analysis of the air trapped in ice cores from Antarctica. This analysis has provided accurate data on the evolution of CO_2 in the atmosphere over the last 800,000 years (Figure 1d) ([36] and references therein). During this time, the Earth's climate has cycled repeatedly from glacial periods typified by much lower global temperatures and expanded ice-sheets over the continents and poles, to interglacial, warm periods similar to the present Holocene. Over the 800,000 years of the dataset, there is a tight association of temperature and CO_2 concentration, with high concentrations during interglacials and low concentrations during glacials.

The $\delta^{11}B$ paleo-pH-meter has recently been used in a series of studies to detect the limits of pH variability at the

sea surface and at depth over glacial–interglacial time-scales [37–41]. These reconstructions, together with data derived from the ratio of B/Ca in foraminifera, which tracks surface and deep water pH and/or $[CO_3^{-2}]$ [28,39,42,43], suggest that the pH of water on the ocean surface was lower during interglacials (high levels of atmospheric CO_2), and higher during glacial periods (low levels of atmospheric CO_2) (Figure 1d). Typical surface water glacial to interglacial pH values have varied between 8.3 units and 8.1 units.

The current human-induced perturbation of seawater pH starts at the low end of glacial–interglacial pH variability. From this perspective, and given that the surface oceans have already acidified by ∼0.1 pH units since the pre-industrial period, current conditions are already more extreme than those experienced by the oceans during glacial–interglacial cycles (Figure 2). Moreover, by the end of the twenty-first century, the projected decline in seawater pH might be three- times larger than perturbations observed as the Earth's climate has oscillated between glacial and interglacial periods. Reconstruction of glacial–interglacial variability in seawater pH also provides an important context for the rate of recent anthropogenic changes. In this respect, changes in seawater pH likely to be observed during this century will probably occur ∼100- times faster than during glacial terminations, which are the periods of time when globally averaged surface seawater pH changed fastest over the last two million years (e.g. [2]). This rate of increase far exceeds the regulation capability of natural Earth system feedbacks to restore the system to pre-industrial conditions, suggesting that the perturbation in ocean chemistry from the release of CO_2 from fossil fuels might last hundreds of thousands of years into the future [44]. It also highlights

the overwhelming challenge that faces the biology of the ocean in terms of adapting to changes which are several orders of magnitude greater than any seen over the past several million years [5].

Changes in other parameters associated with the CO_2 system in seawater will also accompany changes in pH. For example, $[CO_3^{-2}]$ will reach less than half the concentration present before industrialisation in 1750 (Figure 2, Box 1). There is now a wealth of information which outlines a strong reliance of marine calcifiers on $[CO_3^{-2}]$. In this respect, there is evidence from shell weights of foraminifera over glacial–interglacial periods which suggest a thickening of shells during glacial times (i.e. when $[CO_3^{-2}]$ were higher; [45]). However, other factors such as temperature, nutrients, water stratification or a change in optimum growth conditions might also have had a role in controlling calcification in foraminifera ([46] and references therein).

Glacial–interglacial pH is also highly depth-specific, with different changes to pH and $[CO_3^{-2}]$ occurring above and below water depths of ~2.8–3.2 km [28,38,43]. Above this depth, glacial pH and $[CO_3^{-2}]$ were higher than interglacial values but, below this depth, the opposite occurred. This is consistent with the idea that glacial deep Atlantic Ocean waters are more influenced by the deep waters derived from the Southern Ocean, which are characteristically rich in nutrients but low in $[CO_3^{-2}]$. Reconstructing the CO_2 system in deep waters over glacial–interglacial timescales is important, for instance, in knowing if the narrow range of deep- water pH variability that characterises modern oceans (Box 4) also existed at glacial–interglacial scales. This would have implications for the capability of adaptation of benthic species.

Constraining seawater pH and other parameters of the CO_2 system in seawater at different depths is also critical to further understand the processes and drivers of the glacial–interglacial variations in atmospheric CO_2. After more than two decades of research, multiple mechanisms and hypotheses have been proposed to explain these CO_2 fluctuations. However, the exact mechanism or, more likely, combination of mechanisms, still remain elusive (e.g. [47]). Further research on this issue is critical, particularly to validate, calibrate and improve the climate and biogeochemical models which are to provide information on future rates of oceanic absorption of CO_2 and ocean acidification. Several important ocean–climate feedbacks are still pending appropriate representation in such models [48].

Changes during the Cenozoic era (last ~ 65 million years)

Reconstructions of marine calcification using $\delta^{11}B$ and B/Ca in foraminifera over longer periods of time reveal that the typical seawater pH variability of glacial–interglacial cycles, which have paced the Earth over the last ~2 million years, extend to the last ~20 million years at least [32,41]. Only by going back this far do we find conditions similar to those that exist today (Figure 2). Perhaps it is even more sobering to realise that pH conditions that are projected for the end of the twenty-first century are found at only much older periods of time, probably beyond ~40

million years ago [32,49]. Given this, it becomes extremely important to explore these longer timeframes.

Several short-lived warming events, or 'hyperthermals', occurred during the first two epochs of the Cenozoic era (which covers the last ~ 65 million years). These have been linked to possible acidification [50–52], although quantification of the pH change through $\delta^{11}B$ or other proxies is pending. Short pulses of CO_2 in the atmosphere appear to have occurred during these events, with a magnitude comparable with the anthropogenic carbon currently being released by humans *via* the combustion of fossil fuels. Quantifying the causes and consequences of these events, particularly on marine biota and ecosystems, should provide valuable insights into the possible effects of the current human perturbation of the carbon cycle.

The most marked and well studied of these events is the Paleocene-Eocene Thermal Maximum (PETM), which occurred ~55 million years ago. During this event, global temperatures increased by >5 °C over <10,000 years, in synchrony with a massive release of carbon into the atmosphere [50,51]. At that time, the calcite saturation horizon (the depth of the water column above which calcium carbonate can accumulate) might have become shallower by >2 km [50]. Although the exact origin of this carbon is not completely understood [53], a rapid release and oxidation of methane from marine sediments could have been the main cause. A clear drop in the carbonate content of deep- sea sediments directly points towards ocean acidification as a side effect [50,51], a perturbation to the carbon cycle that lasted about 170,000 years [54]. This change involved a series of biological responses, including the mass extinction of benthic foraminifera (e.g. [55]). Surface-dwelling marine organisms seem to have been less affected, although the abundances of calcareous nanoplankton were reduced, and malformations and even extinctions of these species have been reported [56,57]. Differences in the rate of evolutionary change have also been documented, with an increase in the number of extinctions and originations during the PETM [58]. Although some of these changes could be attributable to low pH conditions, they are more likely to be the result of an interplay of changes in multiple environmental factors (e.g. temperature, nutrient availability, oxygen content) that, together with pH, resulted in stressed, unstable and modified marine environments [57,59]. Interestingly, recent model simulations comparing PETM with present conditions forecast higher rates of surface ocean acidification and environmental change in the near future [60].

The 'big five' extinctions (last ~ 500 million years)

Recent studies that have looked further back in the geological time highlight the role of global ocean acidification in the most dramatic five extinction events that the Earth has experienced during the Phanerozoic era. A recent review on the possible causes of these extinctions concludes that, when considering the extent of destruction of coral reefs and their recovery patterns as recorded in the fossil record, only those causes that involve a major perturbation in the carbon cycle remain feasible ([61] and references therein). In particular, there is a strong

correlation between major extinction events on coral reefs, subsequent 'reef gaps' (absence of coral reefs for several million years) and rapidly increasing or high levels of atmospheric CO_2, driving ocean acidification.

Studies focused on specific extinction events have reached similar conclusions. Knoll *et al* [62] thoroughly reviewed the patterns of mortality during the end-Permian mass extinction (251 million years ago). They argued that hypercapnia, the physiological effects of elevated CO_2 concentrations, best accounted for the selective survival observed in the fossil record, although probably in synergy with other perturbations such as global warming, anoxia and/or H_2S poisoning. At the Triassic–Jurassic boundary (205 million years ago), a sudden rise in the levels of atmospheric CO_2 due to volcanic activity or destabilization of methane hydrates coincided with a major suppression of carbonate sedimentation, very likely related to ocean acidification [63]. Organisms made of the most vulnerable forms of aragonite and high-magnesium calcite were most affected. Calcareous phytoplankton were particularly affected, whereas organic-walled phytoplankton seemed to have benefited from the event [64]. A similar situation also occurred during the Cretaceous–Tertiary extinction event (65 million years ago). Most of the planktonic calcifying species became rare or disappeared, but diatoms and dinoflagellates survived ([65] and references therein). These past responses highlight the possibility of future shifts in phytoplankton species from anthropogenic acidification.

In addition to high levels of CO_2 and acidification, changes in the content of Mg and Ca in seawater, controlled by plate tectonic activity, might have modulated biomineralization over the last 450 million years [66,67]. During periods of time when Mg/Ca levels in seawater were >2, the precipitation of aragonite structures was favoured, whereas during periods of low Mg/Ca, calcite precipitation predominated. This would explain, for example, the expansion of reefs during the Oligocene era (34 to 23 millions ago) coinciding with the last significant rise in seawater Mg/Ca to present levels, which are close to 5 [66].

Also regarding coral reefs, there are suggestions that specific biotic controls would have been more important than changes in the chemistry of seawater such as acidification or the Mg/Ca ratio. In a recent review, Kiessling [68] noted the important role that competition for space dictates in the development and evolution of coral reefs. The difficulties of sessile organisms in establishing themselves in stable substrates could have been relaxed upon the advent of photosymbiosis, which would have allowed corals to expand and grow in nutrient-depleted waters.

Overall, these studies highlight the importance of investigating the main drivers of these past catastrophic events to understand how similar changes projected to occur in the near future will influence events in marine and terrestrial ecosystems. This is a valuable way to address issues such as the capacity of marine organisms to adapt to ocean acidification. Due to the obvious constraints, experimental studies are, by definition, limited in their capacity to provide perspectives on the longer-term evolutionary adaptation of organisms to these types of changes. For this reason, paleo-reconstructions provide particularly important perspectives on past, current and future global challenges to the biosphere.

Evidence of impacts observed in the field

Field evidence of the impact of ocean acidification on marine organisms has been limited due to the complexity of the measurements of the parameters of the seawater CO_2 system and the inherent multifactorial nature of the changes that are occurring as a result of rising levels of atmospheric CO_2. Two recent studies have assessed the possible effects on foraminifera, and have observed a recent shell thinning that is probably attributable to ocean acidification. In the first study, shells collected in sediment traps during the years 1997 to 2004 south of Tasmania, Australia, were found to be significantly lighter than those in pre-industrial Holocene deep- sea sediments from the same area [69]. The second study combined foraminiferal shell weights and ^{14}C and ^{13}C analyses from a sediment core in the Arabian Sea, and also found a progressive thinning of foraminifera shells throughout the twentieth century [70]. However, this latter work is confounded by the possible influence of changes to seasonal upwelling.

These results contrast with reports of an increase in the average mass of coccoliths over the past 220 years in the subpolar North Atlantic [71]. However, a more detailed study of the same sediment core showed that the increase in coccolith mass occurred only in larger coccolithophore species [72]. Small species showed a decreasing trend in shell mass, which further emphasizes important differences that can occur between species.

Recent studies examining extension and calcification rates and the density of growth bands within coral records have provided evidence for a decline in calcification since the 1990s [73–75]. Ascribing this decline unequivocally to ocean acidification is difficult, but identification of this trend across a wide array of habitats suggests the involvement of a global factor such as the acidification or warming of the oceans, rather than local factors such as water quality. Disentangling the effect of steadily rising sea temperatures is more difficult given that optimal temperatures for calcification lie below that of the maximum temperature in the summer (e.g. [76]). For this reason, periodic coral bleaching [77] is likely to have also compromised the rate at which corals can calcify [74]. Ecosystem studies of coral reefs (e.g. [78]) have confirmed a clear dependence between community calcification and the aragonite saturation state and temperature. These field observations have led to the development of empirical estimations which project a serious decline in the ratio of calcification relative to physical and biological erosion, with the prospect of coral reefs eventually beginning to crumble and dissolve when atmospheric CO_2 concentrations reach between 450 parts per million by volume (ppmv) [5] and 560 ppmv [79].

The impacts of ocean acidification have also been reported in exceptional environments such as around submarine volcanic CO_2 vents. Studying the areas affected by this phenomenon has the potential to provide insight into the long-term effects of ocean acidification not only on single species, but also on the whole ecosystem. For example, around the Italian Island of Ischia, a clear

reduction has occurred in the number of calcifying species (corals, urchins, bivalves, coralline algae) in the low- pH areas close to CO_2 vents [80,81]. Interestingly, seagrasses and brown algae appeared to thrive under these conditions, probably due to the higher CO_2. Some estuaries also present a range of pH variability which makes them useful for studying whole- ecosystem and long-term acidification effects (e.g. [82]), although the generally large gradients in salinity might confound interpretations.

Conclusions

The accumulating knowledge of past changes in pH from instrumental time-series and paleo-proxies is providing important contextual information with which to understand the environmental magnitude of the current progressive acidification of the oceans. A decrease in ocean pH is already measurable across several instrumental time-series. Contemporaneous temporal and spatial variability exists in seawater pH. Over the last centuries, reconstructions of seawater pH in coral reefs have also shown a certain degree of inter-decadal variability, which provides insight into the natural pH ranges within which marine calcifiers live. In a similar way to global warming, progressive changes in ocean pH will be superimposed on this natural variation in pH and carbonate chemistry, exacerbating the effects heterogeneously in time and space.

A series of paleoceanographic proxies for key parameters of the CO_2 system in seawater, including pH, are available. They help constrain estimates of how seawater chemistry changed in the past. This, in combination with the description of associated ecological changes, is providing useful information which will aid understanding of the likely nature of future changes. Glacial–interglacial seawater pH has changed in harmony with CO_2 levels in the atmosphere. This knowledge places into context the changes we are facing today, in pCO_2 and in pH, which are happening $\sim$100- times faster than during glacial–interglacial transitions. The average surface pH levels that oceans have reached today are already more extreme than those experienced by the oceans during the glacial–interglacial changes and beyond, probably being more extreme than at any time during the last 20 million years. Ocean pH levels that might be reached by the end of the twenty-first century are unprecedented in at least 40 million years.

Changes over different organization levels from marine organisms to ecosystems have been documented in association with past changes in seawater pH. For example, foraminifera seem to have grown thicker or thinner shells over glacial–interglacial timescales, depending on $[CO_3^{2-}]$ and pH. It is significant that marine calcifiers such as benthic foraminifera experienced a massive extinction during the PETM, a catastrophic event that occurred 55 million years ago, which involved extensive ocean acidification, particularly in the deep ocean. Perturbations of the carbon cycle (including ocean acidification) might also have been important (probably in synergy with other effects) in causing the damage associated with the 'big five' extinctions. Records of the most recent past from deep- sea sediments and corals are starting to provide evidence of

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Box 5. Areas of future research

1. Paleo-reconstructions represent an important means by which to place current changes in the global ocean into the context of longer time periods. Paleo-proxies provide an important tool in this regard and, while several have been developed, there is a need to develop and refine further technologies that will allow greater insight into how conditions have changed. These tools need to be combined with those investigating how biological parameters such as species diversity and calcification have changed during past periods of global change.

2. More globally distributed instrumental monitoring stations for ocean chemistry are needed, not only for open ocean (e.g. ALOHA, BATS and ESTOC stations) but for coastal areas.

3. There is a growing number of studies that demonstrate the impacts of ocean acidification on biological systems under field conditions, but these studies remain limited in the spatial and temporal scale. For this reason, there is an urgent need to increase efforts to monitor changes occurring in biological systems as a result of ocean acidification. Importantly, these studies need to uncouple the confounding influence of variables such as temperature from those associated with ocean acidity.

4. There is an urgent need to improve our understanding of the ecosystem- scale ramifications of ocean acidification and associated global changes to predict impacts on primary productivity, food webs and the carbon cycle in general.

5. There is now considerable information on the chemical and biological impacts of ocean acidification, but our understanding of the socio-economic costs is limited. In this respect, there is a substantial need to improve our understanding of the impacts of ocean acidification on human livelihoods and national economies. Detailed economic analyses of the impact on fisheries and other industries such as tourism is vital. These analyses will also provide important information on true costs and consequences of acting or not acting to reduce global emissions of CO_2 and other greenhouse gases.

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effects of the current ocean acidification in the field. Foraminifera seem to have been growing thinner shells during the last decades or century, and reef- building corals are showing decreases in calcification.

In the light of the information provided in this review and the serious consequences anticipated from continued ocean acidification, we highlight a selection of research needs in Box 5. These research requirements will be important for extending our understanding of past changes so that we may understand the implications and consequences of the current unprecedented rate of ocean acidification.

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