REVIEW

Anthropogenic modification of the oceans

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Human activities are altering the ocean in many different ways. The surface ocean is warming and, as a result, it is becoming more stratified and sea level is rising. There is no clear evidence yet of a slowing in ocean circulation, although this is predicted for the future. As anthropogenic CO_2 permeates into the ocean, it is making sea water more acidic, to the detriment of surface corals and probably many other calcifiers. Once acidification reaches the deep ocean, it will become more corrosive to $CaCO_3$, leading to a considerable reduction in the amount of $CaCO_3$ accumulating on the deep seafloor. There will be a several thousand-year-long interruption to $CaCO_3$ sedimentation at many points on the seafloor. A curious feedback in the ocean, carbonate compensation, makes it more likely that global warming and sea-level rise will continue for many millennia after CO_2 emissions cease.

Keywords: ocean; Anthropocene; ocean acidification; global warming; stratification; carbonate gap

1. Introduction

The ocean is being changed by human activities in many ways. Here, the focus is on global scale rather than local changes, and specifically on changes to the Earth System as a whole rather than simply those that are human-relevant (so, for instance, overfishing and pollution are not covered). An additional emphasis is on those ocean changes that will leave an imprint in the sedimentary and/or fossil record. Many reviews consider only the next 100 years; here, longer term consequences are also considered. The main changes reviewed here are shown in figure 1.

(a) Rise in atmospheric CO_2

Overpopulation is the major underlying reason for the large magnitude of anthropogenic impacts, including the rise in atmospheric CO_2, which is behind many of the observed and predicted changes to the ocean. Technological choices are also obviously highly important, with overpopulation magnifying the consequences of those choices. From bubbles trapped in ice cores, we
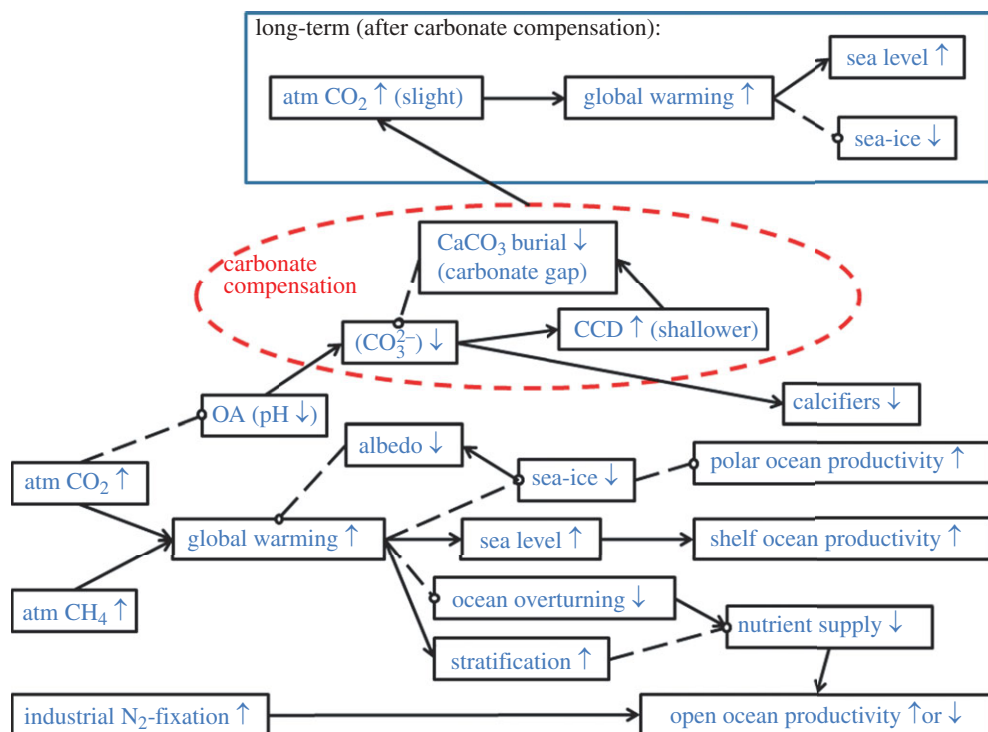
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Figure 1. Schematic showing some major changes to the ocean arising as a result of human impacts. A solid arrow between two boxes indicates a positive influence, whereby an increase in the value of the forcing variable leads to an increase in the value of the dependent variable. Conversely, a dashed line ending in an open circle indicates a negative influence (increase leads to decrease). Upward arrow within a box indicates a tendency for human influences to increase this property, Downward arrow within a box indicates that it is more likely to decrease. The red dashed line encloses the negative feedback loop that is carbonate compensation, which will lead to a prolonged slight elevation of atmospheric CO_2 and climate (top section). CCD, carbonate compensation depth; OA, ocean acidification.

know that the atmosphere contained approximately $280 \, \mu atm$ of CO_2 prior to the Industrial Revolution, and that this concentration was fairly stable over thousands of years prior to that, ever since the large rise following the last ice age, when there was approximately $180 \, \mu atm$ of CO_2 in the atmosphere. Since the 1950s, regular measurements have been made at the Mauna Loa Observatory in Hawaii and at the South Pole, revealing a year-on-year rise in CO_2. When the observations began, CO_2 was already at approximately $315 \, \mu atm$ and rising by between 0.5 and $1 \, \mu atm$ per year. Now, in 2010, the concentration is approximately $390 \, \mu atm$ and rising by about $2 \, \mu atm$ per year (there has been a slight reduction in the rate of increase over the last few years, owing in part to the global economic recession). The atmospheric CO_2 concentration is now measured concurrently across a large network of sampling stations distributed around the globe (http://www.esrl.noaa.gov/gmd/ccgg/trends/#global).

Human activities have therefore already added more than $100 \, \mu atm$ of CO_2 to the atmosphere, i.e. more than the difference in atmospheric CO_2 between ice ages and interglacials. Various scenarios of future societal behaviour and future

CO_2 emissions are employed to help estimate how the level of atmospheric CO_2 may vary in the future. While it is to be hoped that the rise in CO_2 will come under control, it is also pertinent to note that CO_2 levels at this time are currently exceeding even the more pessimistic earlier projections (i.e. exceeding those of the IS92a 'business-as-usual' scenario [1]). At the same time as CO_2 has increased in abundance in the atmosphere, so too have the concentrations of other greenhouse gases such as methane and N_2O.

The main human activities producing CO_2 are the burning of fossil fuels (coal, oil, gas), but also the manufacture of cement. Changes in land use, including deforestation, have also contributed large amounts. Of the CO_2 emitted between 1959 and 2006, it is estimated that 43 per cent remains airborne, 28 per cent entered the oceans and 29 per cent was sequestered by new growth of terrestrial vegetation [2].

2. Global warming

The most well known of the effects of elevated CO_2 and other greenhouse gases is the increased interception of outgoing (potentially planet-leaving) infrared radiation. This understanding was originally underpinned by measurements of the amounts of heat radiation penetrating through tubes with different gas compositions. The increase in greenhouse gases thus changes the radiation balance of the Earth such that the previous steady state is disturbed: more radiation now reaches the Earth surface than is lost from it, and it consequently warms up, i.e. global warming. The evidence basis for global warming is now rather strong and includes ground-level thermometer-based measurement records since 1850. Closer to the present day, the data record now includes measurements up through the atmosphere, down through the sea, down into the Earth (boreholes) and from satellites looking down at Earth. When these modern records are joined to proxy records (such as from ice cores) of temperatures over the last several thousand years, the current warming can be put in the context of past natural variability. The wealth of evidence for global warming is both diverse and compelling. It is estimated that, averaged across the globe, air temperature at the surface of the Earth rose by 0.75°C during the twentieth century [3]. A further rise of between 1.1 and 6.4°C is projected for the twenty-first century [3], with uncertainties deriving in part from uncertainties in future emissions, and in part from incomplete knowledge about how the Earth System will respond to them.

Global warming is also evident in compilations of many millions of vertical profiles of sea water temperature collected over the last 50 or 60 years [3–6]. The data suggest that the top 300 m of the ocean warmed by about 0.2°C on average between the mid-1950s and the mid-1990s. The ocean is also warming.

(a) Ocean heat sink

Water has much more 'heat inertia' than air, however. The volumetric heat capacity of sea water is about $4\,\mathrm{J\,cm^{-3}K^{-1}}$, compared with about $0.001\,\mathrm{J\,cm^{-3}K^{-1}}$ for air at sea level. Three orders of magnitude more energy input is required to raise the temperature of a cubic metre of sea water than a cubic metre of air. The heat capacity of the total ocean is also about 1000 times that of the total atmosphere. More than 80 per cent of the extra heat retained up to now by the

stronger greenhouse has entered the ocean. Because more heat needs to be put in to heat water, the heat inertia of the oceans introduces a time lag into the global warming response to elevated greenhouse gases. In the same way that it takes radiators time to heat up a cold room (and takes them even longer to heat a room containing a swimming pool), we have not yet experienced all of the heating that will eventually be associated with the current radiation imbalance. Over the next century, for instance, we are probably already committed to a further approximately 0.5°C of climate change. Even if emissions cease today, or if the level of greenhouse gases in the atmosphere is stabilized, global warming will continue for decades to come, mainly because of the slow response of the ocean [3,7].

(b) Sea-level rise

As sea water warms, it expands slightly (thermal expansion) leading to sea-level rise. Melting of land-based ice as climate warms also contributes to sea-level rise, as more water is added to the ocean. Changes in sea level in the recent past are quite well monitored through a network of tide gauges and more recently satellite altimetry. While the amount of sea-level rise that has already occurred (17 cm in the twentieth century; [3]) and the rise that is predicted by year 2100 (perhaps another 20–60 cm if ice-melt is assumed small [3], or perhaps more than a metre if significant ice-melt occurs [8]) both seem relatively modest, they could still lead to flooding of large tracts of low-lying land. Areas potentially at risk include coastal floodplains such as the Ganges Delta and land reclaimed from the sea.

The amplitude of sea-level rise will be much greater if the large land-based ice-sheets (those on Greenland and Antarctica) melt. Melting of the Greenland ice-sheet, for instance, would add 7 m of sea-level rise; melting of just part of the Antarctic ice-sheet, the West Antarctic ice-sheet, would produce a further approximately 5 m of sea-level rise; melting of all ice sheets would add about 64 m to sea level. It seems more likely that these latter, very large amounts of sea-level rise will eventually occur when we take into account the expected long-term persistence of high CO_2 and warming (§5).

Sea level is estimated to have been 4–6 m higher than now during the Eemian (last interglacial), when temperatures were 1 or 2°C warmer than now [9]. It was approximately 120 m lower than now towards the end of the last ice age. A geological manifestation of a prolonged and high-amplitude sea-level rise could be a surge of upward growth of corals and an unusually high rate of $CaCO_3$ accumulation on reefs, according to the prevailing theory of atoll formation. Surface corals and coralline algae, including those in atolls, fringing reefs and barrier reefs, should respond to increased submergence with increased growth, if they have not previously been rendered scarce by ocean acidification (OA) and bleaching events (§3).

(c) Reduced ocean overturning

Computer models of the physics of ocean overturning have mostly agreed that global warming is likely to lead, eventually, to shutdown or weakening of ocean overturning ([3,10]; see also [11]). As the temperature of surface waters increases, their density decreases and they become more buoyant compared

with deeper waters whose temperature remains largely unchanged. Additions of low-salinity water to the locations where surface water usually sinks to depth (traditionally considered the starting points of the thermohaline circulation) also lower density and inhibit sinking. It has therefore been thought likely that, if CO_2 emissions continue at current rapid rates, ocean overturning will eventually slow. At the present time, a more complex picture is emerging, however. The previous understanding of how the rate of global overturning is controlled is being challenged (e.g. [12,13]). More recent work emphasizes the role of alternative factors (such as the need for dissipation of tidal energy on Earth, or the influence of eddies and winds; e.g. [14]) in controlling overturning rates. There is therefore at the present time substantial uncertainty surrounding mechanisms by which the overturning circulation could be weakened.

Since 2004, an array of instruments has been stretched across the North Atlantic at 26°N, purposefully deployed in order to look for evidence of a slowing in the overturning circulation, but no compelling evidence has been found to date. Summarizing over all the evidence obtained so far, including from the instrument array, there is as yet no clear or coherent evidence for a slowing trend [3,15].

If deep water does cease to form in the northern North Atlantic, it is argued that warm surface waters will no longer be pulled so far north to replace them, and a cooling of the high-latitude North Atlantic will result. Because of the enormous warming effect that this ocean heat transport has on the overlying air (partly because of the large difference in heat capacities discussed earlier), it is likely that the climate in western Europe and some of the other land adjacent to the North Atlantic would be cooled by several degrees if the ocean heat transport stopped. It is thought [16] that this happened during the Younger Dryas event that interrupted the great warming following the last ice age. Other episodes of abrupt climate change in the past may also have been caused wholly or in part by changes to the rate of ocean overturning. If a slowing of ocean overturning is the main factor, we would expect associated climate impacts to be strongest in the northern hemisphere. Results from ocean drilling have been interpreted as showing that ocean circulation patterns have changed on Earth before, such as at the Palaeocene–Eocene thermal maximum (PETM) event [17]. Among various computer modelling studies, there is a consensus that that there is likely to be hysteresis to any shutdown ([3]; although see also [11]). In other words, if ocean overturning shuts down at a temperature X, it is unlikely to start again until the oceans warm back up to a temperature considerably higher than X.

(d) Stratification

A major source of nutrients to surface waters in many parts of the world is the vertical mixing between water at the surface and water slightly further down. Because there are more nutrients in deeper water (surface waters are often almost completely stripped of nutrients), exchange of surface and deep waters generates a net upward flux of nutrients. Stratification is the separation of a liquid into vertically stacked layers of different density, for example when the vinegar and oil in French dressing separate into different layers. During sunny periods, the Sun's heat warms up surface waters of the ocean, reduces their density (hot water is lighter than cold water) and makes the lighter waters then float on top of the

denser colder waters below. Stratification is important for marine life because it tends to inhibit vertical mixing, and thereby shuts off nutrient supply to the phytoplankton at the base of the food chain.

It was predicted some time ago that global warming would lead to a modest (−6%) reduction in marine export production (the rate at which material sinks out of the surface ocean), primarily because of increased stratification [18]. While analyses of satellite ocean colour data (e.g. [19]) support such a conclusion, the main dataset used is only 12 years long (the SeaWiFS time series started in 1998). It has also been noted [20] that the satellite-observed trends in chlorophyll (phytoplankton) correlate strongly with regional oscillations in climate variability with periods of more than 10 years, such as the Pacific Decadal Oscillation. While these correlations with regional climate indices are fully consistent with climate forcing phytoplankton through stratification, it is also the case that satellite datasets are probably not yet of sufficient duration to allow definitive separation of a global warming-associated trend from natural variability [21]. The most recent development is an analysis [22] of over 70 years of direct measurements of chlorophyll concentration and sea water transparency (high phytoplankton concentrations make sea water more turbid, or in other words decrease transparency, so chlorophyll and transparency are strongly inversely related). These data circumvent the problem of limited duration of satellite data. They also suggest a declining chlorophyll trend over time in many ocean basins, attributed to global warming.

Although data suggest an ongoing decline, the more alarmist predictions of dire consequences of global warming on ocean productivity (e.g. [23]) are unlikely to come to pass. Very warm Cretaceous oceans were apparently rather productive, sustaining for instance the largest teleost fishes in the fossil record (*Xiphactinus*, up to 5 m long), giant swimming reptilian pleiosaurs (up to 10 m) and mosasaurs (some longer than 15 m) [24]. Thick chalk deposits, formed from shells of plankton, were also laid down in warm Cretaceous seas. It is not clear whether climate will be less influential on ocean fertility once deep waters also warm in response to climate (it takes about 1000 years for the whole ocean to turn over).

(e) De-iced polar oceans

At the time of writing, it has been established that the ocean as a whole is warming, but there are less data on which to base statements about geographical differences in that warming. However, on theoretical grounds we can confidently expect that some parts will warm faster than others. Areas where ice is melting away, for example, are likely to warm more rapidly. Global warming is melting away ice, causing reflective white sea ice to be replaced by dark, heat-absorbing sea water. The large change in local albedo leads to a large change in the amount of local heating, exacerbating the initial warming. This ice–albedo positive feedback (which also occurs, to a lesser extent, on land: snow–albedo feedback) amplifies warming and makes warming more rapid in the Arctic Ocean [25].

The melt-back of ice is taking place at a dramatic rate in the Arctic Ocean. The area covered by sea ice in late summer declined by 7 or 8 per cent per decade between 1953 and 2006, and at an even faster rate than that in the more recent decades [26]. No significant decline in sea-ice extent is observed so far in the Southern Ocean, however.

Unlike melting of land-based ice, melting of floating ice has only a small effect on sea level (e.g. [27]). But it has its own consequences. For a start, ice is only partially transparent to sunlight, and thick sea ice prevents phytoplankton growth beneath. A reduced spatial extent and shorter seasonal duration of sea ice can be expected to open up new areas for colonization by phytoplankton, extend 'growing seasons' and to stimulate greater annual phytoplankton production [28]. The Arctic Ocean in particular is likely to undergo a complex set of changes in coming decades, although it will not come to resemble the 'Azolla Event' of 50 or so million years ago, when very large blooms of the free-floating fern *Azolla* fell into Arctic Ocean sediments [29]. The Arctic at that time was fresh or brackish, because it was mostly cut off from the other oceans.

3. Ocean acidification

The first major effect of increased CO_2 has just been discussed, the second is OA. It is sometimes referred to as 'the other CO_2 problem' [30]. At the time this is being written, several large national and international research programmes into OA have recently started or are due to start shortly. A summary of our current knowledge is given here, but the intensity of current research in this swift-moving field makes it likely that there will soon be further advances. As mentioned above, approximately 28 per cent of the CO_2 that has been emitted to Earth's atmosphere now lies in its oceans, where it perturbs the carbonate chemistry of sea water. OA concerns the nature of the carbonate chemistry changes (including lowering of pH), and the impact those changes have on organisms, ecosystems, biogeochemical processes and other aspects.

(a) The chemistry of ocean acidification

The chemistry of OA is relatively simple and straightforward. As anthropogenic CO_2 enters sea water, it combines with water to form carbonic acid (H_2CO_3, present in negligible concentrations), which in turn dissociates to form bicarbonate ions (HCO_3^-) and carbonate ions (CO_3^{2-}), according to

$$CO_2(aq.) + H_2O \leftrightarrow H_2CO_3 \leftrightarrow HCO_3^- + H^+ \leftrightarrow CO_3^{2-} + 2H^+$$

Most of the added CO_2 ends up as HCO_3^-, with a side effect being the release of a proton (H^+ ion) to the surrounding sea water. It is this that lowers pH ($= -\log_{10}[H^+]$). The sum of the carbon dioxide, carbonic acid, bicarbonate and carbonate ions dissolved in sea water is known as dissolved inorganic carbon (DIC). The relative proportions of these three components vary as pH varies (figure 2). Increasing invasion of CO_2 into sea water leads to an increase in the concentrations of $CO_2(aq.)$ and HCO_3^-, but a decrease in the concentration of CO_3^{2-} (figure 2). Currently, about 91 per cent of DIC in the surface ocean exists as bicarbonate ions, 8 per cent as carbonate ions and 1 per cent as carbon dioxide [31]. All three species of DIC are biologically important and future changes in their concentrations may be large; for instance, a predicted halving of the carbonate ion concentration by the end of the century, if emissions remain relatively uncontrolled.
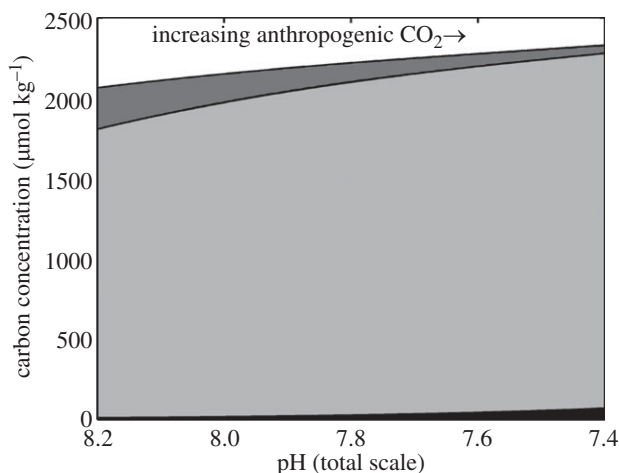
Figure 2. Changes in the concentrations of the three different chemical species constituting dissolved inorganic carbon (DIC). As the influx of extra CO_2 acidifies the surface ocean and raises DIC, the carbonate ion concentration (dark grey) falls strongly, the concentration of dissolved CO_2 gas (black) increases strongly and the bicarbonate ion concentration (light grey) increases slightly. Surface ocean pH was on average about 8.2 in the pre-industrial ocean, is about 8.1 on average today and could drop to as low as about 7.4 if all available fossil fuels are burnt. Graph calculated for an average surface ocean of temperature 15°C, salinity 35 and alkalinity 2310 μmol kg^{-1}. Black-shaded region, $[CO_2(aq.)]$; light grey-shaded region, $[HCO_3^-]$; dark grey-shaded region, $[CO_3^{2-}]$.

The saturation state of sea water with respect to calcium carbonate (Ω) is given by

$$\Omega = \frac{[Ca^{2+}] \times [CO_3^{2-}]}{K_{sp}^*}.$$

Dissolution of mineral $CaCO_3$ takes place when $\Omega < 1$ (undersaturated sea water), and inorganic precipitation is possible at $\Omega > 1$ (supersaturated sea water), although in practice the presence of magnesium and other dissolved substances in sea water inhibits calcification and prevents spontaneous crystallization from occurring under normal surface sea water conditions (Ω_{cal} between 2 and 9; Ω_{arag} between 1.2 and 5).

There are two main forms of $CaCO_3$ produced by marine calcifiers: calcite and aragonite, with corresponding saturation states (Ω_{cal} and Ω_{arag}) that covary but are slightly offset from one another. Owing to its structure, aragonite is more easily dissolved (has a higher K_{sp}^*) and therefore $\Omega_{ar} < \Omega_{ca}$. As the calcium concentration is relatively invariant through the oceans and largely unaffected by human activities, and K_{sp}^* (the solubility product) is relatively constant year on year at a given point in the ocean, Ω varies primarily with $[CO_3^{2-}]$.

Model reconstructions have estimated that surface ocean pH has already decreased from a pre-industrial average of approximately 8.2 to 8.1 [32]. Direct measurements also show changes in the pH and carbonate chemistry of sea water.

Decreasing pH and $[CO_3^{2-}]$ and increasing dissolved [DIC] and $[CO_2(aq.)]$ have been observed at the Hawaiian Ocean Time Series, the Bermuda Atlantic Time Series and the European Station for Time Series in the Ocean at the Canary Islands [33–38]. pH measurements on two cruises along the same route between Hawaii and the Aleutian Arc, but 15 years apart in time, also found lower pH on average during the later cruise [39].

Model predictions suggest that, depending on future emissions, the average surface ocean pH may decrease by 0.3–0.4 units by 2100 [32]. Because of the logarithmic relationship between pH and $[H^+]$, this is approximately equivalent to a 150 per cent increase in $[H^+]$ and will lead to an approximately 50 per cent decrease in $[CO_3^{2-}]$. Caldeira & Wickett [40] estimate a maximum reduction in surface ocean pH of 0.77 units by 2300, if future CO_2 emissions remain high. Although CO_2 is entering surface waters in all parts of the ocean, regardless of latitude, polar waters start off from naturally lower baseline Ω values. Model predictions suggest that large areas of Arctic surface water will start to become undersaturated ($\Omega < 1$, at which point dissolution of $CaCO_3$ is chemically favoured) with respect to aragonite over the next few decades, also in the Southern Ocean shortly after [32,41]. But Ω is also dropping in (sub-)tropical waters.

(b) Impacts on calcifiers

The effects of these chemical changes on marine biology are less well understood. Only a brief summary will be given here, because our understanding is not mature and this subject is being actively investigated at present. The greatest concern is for calcifying organisms (those synthesizing $CaCO_3$ for shells or skeletons), because of the known considerable sensitivity of Ω to anthropogenic CO_2, and because of experimental studies showing effects. A key unknown is the degree to which those species living today will be able to adapt evolutionarily to cope with the chemical changes.

A large body of experimental evidence suggests that OA will dramatically reduce the distribution of warm-water corals (which precipitate aragonite) through lower calcification rates and hence more fragile skeletons. It seems highly probable that coral reef ecosystems will cease to occur naturally on Earth, outside of large aquaria. Almost all experiments agree in finding reduced calcification at higher CO_2 and/or lower pH. To be precise, it is concluded that the governing variable is $[CO_3^{2-}]$ (Ω_{ar}), and therefore that the rate of calcification will decline in sympathy with it (e.g. [42]). A recent study of *Porites* coral from 69 reefs of the Great Barrier Reef found calcification to have declined by 14 per cent since 1990 [43]. However, as temperature, light and nutrients also influence calcification, attributing changes in calcification rate observed in field studies to a single factor is not straightforward [44]. Silverman *et al.* [45] modelled the effect of temperature and Ω_{arag} on calcification rate, based on field observations, to predict the future distribution of warm-water corals. The results were alarming, suggesting that, by the time atmospheric CO_2 reaches $560\,\mu\text{atm}$, all coral reefs will stop growing and start to dissolve [45].

Coralline algae are also important calcifiers in shallow-water systems, and major contributors of $CaCO_3$ to reefs. They precipitate high-Mg calcite and are therefore particularly susceptible to dissolution. When crustose coralline algae

were exposed to elevated CO_2 in mesocosms, their recruitment rate and growth rate were severely inhibited and the percentage cover of non-calcifying algae increased [46]. Semesi *et al.* [47] found that calcification in the coralline alga *Hydrolithon* decreased following an increase in the dissolved CO_2 concentration. Epiphytic coralline algae are much less abundant in low-pH water near to a CO_2 vent [48]. These and other studies suggest that, like corals, coralline algae will be highly susceptible to future increases in atmospheric CO_2.

Calcification rates of many other benthic calcifiers such as cold-water corals, echinoderms, bivalves and crustaceans are likely to also be detrimentally affected by OA, although results of a wide-ranging study strongly suggest that not all taxa will calcify less [49].

Calcification in foraminifera (e.g. [50]) and pteropods [32] will most probably be negatively affected by OA. Calcification in coccolithophores may also be affected but the evidence is far from conclusive. From experimental studies, there is considerable disagreement about the magnitude or even the direction of the change (e.g. [51,52]), even between experiments on nominally the same species [53]. Data from seafloor sediments show increasing coccolith mass accompanying rising pCO_2 since the Industrial Revolution [52,54].

Studies of coccolithophore biodiversity through the PETM, a palaeo-acidification event when many benthic foraminifera went extinct, show increased turnover but no decline in biodiversity of coccolithophores [55,56]. Coccolithophores also mostly survived the high-CO_2 oceanic anoxic event (OAE) 1a,[1] although some changes in size and assemblage occurred [57]. The great success of coccolithophores through the Cretaceous as a whole is not relevant to evaluating their fate under OA. Even though CO_2 levels were much higher at this time, there was more calcium in the oceans (e.g. [58]) (raising Ω independently), and carbonate compensation depth (CCD) records show that ocean $CaCO_3$ saturation was not especially low [59].

Even if OA strongly reduces the strength of the inorganic carbon pump through inhibiting pelagic calcification, the positive feedback on atmospheric CO_2 is surprisingly small (not more than approx. $10\,\mu$atm) over the course of the next century [60,61], although the feedback becomes increasingly important the longer the inhibition continues [62].

(*c*) Other possible consequences

Many other possible side effects of OA are being investigated. Animal metabolisms may be affected as more energy needs to be used for internal acid–base regulation. Early life stages of fishes may be vulnerable. A number of studies now show that N_2 fixation by the marine species *Trichodemium* appears to be fertilized by high CO_2 [63–67]. Photosynthesis may also be fertilized by the extra CO_2 availability, in some groups at least. OA may affect marine organisms indirectly through changes in nutrient and metal speciation (e.g. [68]) and changes in sound propagation.

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[1]OAEs are specific periods in Earth history when the deep ocean became anoxic, leading to the sediments in many places becoming dark in colour due to high organic carbon content (lack of oxygen hinders decomposition). Some of the most pronounced oceanic anoxic events occurred during the Cretaceous, including OAE 1a, which took place about 120 Ma.

4. Carbonate gap

(*a*) *The carbonate compensation depth will become shallower*

A second impact of OA is on the dissolution rather than the precipitation of calcium carbonate. Although some calcifiers surround their $CaCO_3$ with organic membranes, in general dissolution is, unlike precipitation, an inorganic process and therefore occurs in a more predictable fashion. When biogenically produced $CaCO_3$ falls to the seafloor, it generally undergoes one of two fates: it either remains on the seafloor and accumulates there (eventually getting buried and becoming part of newly forming marine sedimentary rocks) or it dissolves. At the present time, nearly all shallow-water benthic $CaCO_3$ persists, but about half of the rain of $CaCO_3$ particles in the pelagic ocean accumulates and about half dissolves [69]. Because of OA, these numbers will change. The ocean is becoming more corrosive to $CaCO_3$, leading over time to a major shift towards dissolution.

For each location on the deep seafloor, the propensity for $CaCO_3$ preservation or dissolution in sediments is governed by whether the seafloor in that location lies above or below the carbonate saturation horizon (CSH; the depth at which $\Omega = 1$). Because of a strong pressure effect, the value of Ω decreases with depth, such that deeper waters are more corrosive to $CaCO_3$. Anthropogenic CO_2 is presently concentrated mostly in the surface of the ocean [70] because it is in intimate contact with the atmosphere. There is currently very little fossil fuel CO_2 in the deep ocean. However, over time as newly formed deep waters take down anthropogenic CO_2 with them, acidification of the deep ocean will proceed. Over hundreds of years, first the deep Atlantic (where a lot of $CaCO_3$ burial takes place today), then the deep Indian and the deep Pacific will undergo great changes in their $CaCO_3$ saturation. The depth of the CSH is very sensitive to the value of $[CO_3^{2-}]$, which in turn is very sensitive to additions of anthropogenic CO_2.

This topic has received little attention, but two computer modelling studies [71,72] both predict a dramatic shallowing of the average depth of the CSH. It is calculated that it will shoal from several kilometres deep at present, to within hundreds of metres of the surface after a few centuries. Changes to the lysocline (the depth at which $CaCO_3$ dissolution becomes apparent in the seafloor sediments) and the CCD (the depth at which dissolution is sufficiently intense to ensure that no, or hardly any, $CaCO_3$ survives in the sediments) are however predicted to be less dramatic, although still large [72]. It can be seen that penetration of anthropogenic CO_2 into the deep ocean over several centuries will lead to a significant reduction in $CaCO_3$ burial in the deep sea.

(*b*) *Reef CaCO$_3$ accumulation will decline*

Reductions in $CaCO_3$ accumulation may not be restricted to the deep ocean, however. The net rate of $CaCO_3$ accumulation in reef settings depends on the excess of $CaCO_3$ formation over $CaCO_3$ dissolution. Comparison between reefs currently sitting in relatively low and relatively high Ω waters suggests that future acidification of surface waters will have large impacts on this balance [73]. It seems likely that in future dissolution will outweigh precipitation on many of these reefs, even without the probable strong inhibitory effect of OA on precipitation. Set

against this, however, is the possibility (§2*b*) that surface coral reefs, if still able to calcify at all in future more acidic oceans, may be able grow and calcify more rapidly as they are stimulated by, and attempt to keep pace with, sea-level rise.

(*c*) Large changes to sediments forming at the bottom of the sea

There are clear implications for the composition of marine sediments. Whereas many of the sediments forming today are predominantly calcareous, such sediments will become rarer in future. Many sediments that today are more than 90 per cent $CaCO_3$ will, for several thousand years (it will take carbonate compensation this long to rectify the $CaCO_3$ undersaturation), change to being formed mainly from clays, opal and other non-$CaCO_3$ particles. As a result, the colour of many marine sediments will change. There will be a hiatus in $CaCO_3$ deposition and coccolith and foram oozes will become scarcer. These predicted changes are of a similar nature to those observed to have taken place in the south Atlantic during the PETM [74], although the Anthropocene carbon addition to the oceans is taking place much more rapidly than occurred at the PETM [75].

The Anthropocene will in this way leave a clear signal buried in some marine sediments. If, many millions of years in the future, cores are drilled through marine sediments at certain palaeodepths, the Anthropocene will stand out as a darker band interrupting the long continuity of lighter coloured $CaCO_3$-rich sediments, as can be seen on land today, in exposed marine sediments dating from the PETM [76].

5. Long persistence of elevated CO_2

It is not always appreciated that the natural long-term response of the Earth System to a large addition of CO_2 is to settle towards a new steady state, one that has slightly more CO_2 than before. Whereas it might be thought that the Earth System would naturally tend, a few centuries after emissions cease, to return back to normal (i.e. pre-industrial), this is not the prediction. There is instead a consensus among most models that the post-fossil steady state will be different [77]. The Earth System will start to converge back towards a new state, one in which the atmosphere contains slightly more carbon dioxide than previously. The post-fossil fuel planet will therefore also converge towards being slightly warmer than it was during the pre-fossil fuel Holocene. The difference between pre- and post-industrial steady states arises because of an unusual feedback in the ocean. Models predict the new steady state will include an atmosphere retaining almost 10 per cent of the extra fossil fuel CO_2 that was emitted to it [77–81].

The reason for the unexpected behaviour is complex, and can only be considered fairly briefly here (for a more detailed explanation, see [79]).

(*a*) Recovery owing to carbonate compensation

The ocean possesses a natural stabilizing mechanism (homeostat) called carbonate compensation [82]. This negative feedback acts to maintain a balance between the input and output of 'carbonate ion' to the oceans. If river carbon

and alkalinity inputs and $CaCO_3$ production in the surface ocean do not undergo major change, then carbonate compensation acts to stabilize the carbonate ion concentration of the oceans (to be completely correct, it stabilizes the saturation state Ω with respect to $CaCO_3$, but, over time scales less than 1 million years, this is controlled mainly by $[CO_3^{2-}]$, because $[Ca^{2+}]$ has a very long residence time of order 1 million years). It stabilizes deep ocean $[CO_3^{2-}]$ but does not stabilize atmospheric CO_2 or $pCO_2(aq.)$, or at least only does so indirectly and imperfectly, as a side effect of stabilizing $[CO_3^{2-}]$. This distinction is important.

The way in which the feedback will take effect has already been introduced in the previous section. Acidification of the deep ocean will lead to a much shallower CCD, a large increase in $CaCO_3$ dissolution and a decrease in $CaCO_3$ burial. $CaCO_3$ deposited on the seafloor in pre-industrial times may also respond to the increased corrosiveness of deep waters by dissolving (a so-called 'burn-down' of $CaCO_3$ is expected to take place, especially where sedimentation rates are slow; [83]). The overall excess of river inputs and dissolution (both supplying 'carbonate ion') over $CaCO_3$ burial (removing 'carbonate ion') will lead to an accumulation in the ocean until deep-sea $[CO_3^{2-}]$ is restored to its previous level.

(b) Effect on atmospheric CO_2

The carbonate chemistry of sea water [84] is a two-degree-of-freedom system, such that knowledge of any two parameters, together with temperature, salinity and pressure (depth), gives all the rest. Therefore, it is possible to calculate the carbonate ion concentration from the conservative (insensitive to fluctuations in temperature and pressure) parameters DIC and alkalinity, as in figure 3a.

Carbonate compensation acts to counteract deviations away from a set-point value of deep-sea $[CO_3^{2-}]$, which has an average value of approximately $100\,\mu mol\,kg^{-1}$ in today's deep ocean [83], with an average of about $200\,\mu mol\,kg^{-1}$ in the surface ocean. In other words, during interglacials, carbonate compensation has presumably ensured that surface ocean chemistry lies somewhere close to the dotted black line in figure 3a. A similar contour plot can be constructed for $pCO_2(aq.)$ (figure 3b). The contours for $pCO_2(aq.)$ are almost, but not quite, parallel to those for $[CO_3^{2-}]$.

In figure 3c, the two sets of contours are superimposed. The equilibrium $[CO_3^{2-}]$ is again indicated. The disequilibrium impact of the invasion of anthropogenic CO_2 is shown (line 1), as also is the restoring influence of carbonate compensation (line 2). What is immediately clear, however, is that the restorative force is not in exactly the opposite direction to the disturbing force. This is why the feedback was described as unusual above. Carbonate compensation will take the ocean back to $[CO_3^{2-}] \approx 100\,\mu mol\,kg^{-1}$ in the deep, approximately $200\,\mu mol\,kg^{-1}$ in the surface, but in other regards will not restore ocean chemistry to anything like the state beforehand. Because the feedback (less burial of $CaCO_3$, more dissolution) adds yet more carbon to the ocean, it in fact exacerbates the original addition of carbon from fossil fuel CO_2 [85]. Carbonate compensation is therefore simultaneously a positive feedback on DIC and a negative feedback on $[CO_3^{2-}]$.
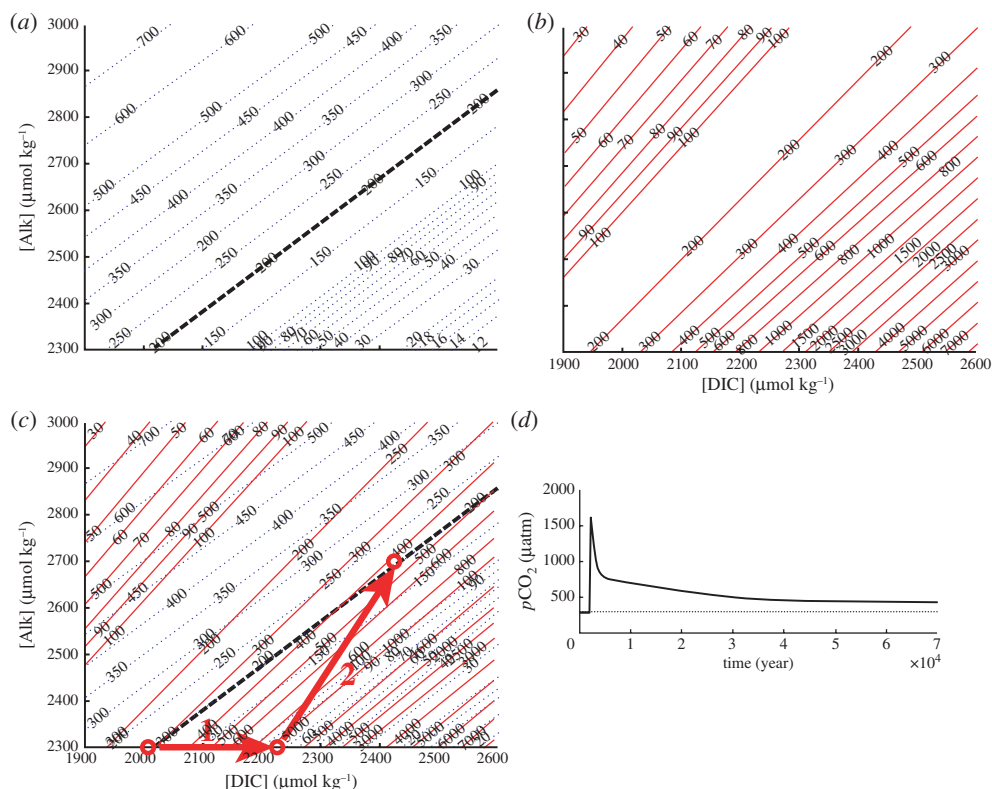
Figure 3. Long duration of high CO_2. (*a*) Carbonate ion contours ($\mu mol\,kg^{-1}$) as a function of DIC and alkalinity for surface waters (pressure = 1 bar) at a temperature of 15°C and a salinity of 35. The dashed line indicates the equilibrium carbonate ion concentration. Note that contour intervals vary. (*b*) Contours of partial pressure of CO_2 as a function of DIC and alkalinity for surface waters (pressure = 1 bar) at a temperature of 15°C and a salinity of 35. (*c*) Plot with both sets of contours shown. Line 1 shows the invasion of 4000 Gt C of anthropogenic CO_2 when distributed evenly throughout the full ocean depth (it adds to DIC but not alkalinity). Line 2 shows the carbonate compensation response (it adds DIC and alkalinity in a ratio of 1 : 2). (*d*) Atmospheric CO_2 over time in a simple ocean and atmosphere carbon model containing the carbonate compensation feedback. Early on in the model run, 4000 Gt C of fossil fuel CO_2 was added in a sinusoidal pulse over 400 years [79]. As in other models, there is no return to the initial value within this time frame.

The end result is that we can expect the ocean to be returned to the $[CO_3^{2-}] =$ $100\,\mu mol\,kg^{-1}$ line in figure 3*a*,*c*, but to a different point on that line from where it started. As can be seen in figure 3*c*, because $[CO_3^{2-}]$ and $pCO_2(aq.)$ contours are not quite parallel to each other, the final point will have a slightly higher $pCO_2(aq.)$ value than the initial one (about $430\,\mu atm$, $150\,\mu atm$ higher than the pre-industrial initial value, if we burn all 4000 Gt C of fossil fuels; see also figure 3*d*).

(*c*) Consequences for long-term climate

The obvious implication is that the planet will not cool down in the same way that it is heating up. If the Earth is 'left to its own devices' to recover from fossil fuel CO_2, then the cooling down will be much slower than the heating up [86].

The cooling will also be incomplete; the Earth will not cool all the way back down to where it started from, at least not unless some other feedback (such as silicate weathering) eventually kicks in to remove the excess CO_2. If it is silicate weathering, then the return to Holocene levels will most probably take hundreds of thousands of years [81]. If the system is geoengineered instead of being left to its own devices, for instance if CO_2 is actively removed from the atmosphere by scrubbers, then a different future behaviour may result.

Some implications, both positive and negative, of the predicted long-term persistence of high CO_2 and warm climates, are as follows:

— eventual melting of all ice sheets is more likely;
— therefore sea-level rise measuring many tens of metres is eventually likely to occur;
— eventual slowdown of the overturning circulation is more likely (§4); and
— the next ice age (or the next several ice ages) may be avoided [87].

6. Other changes

There are many other impacts on the oceans that are being investigated, of varying importance and probability of occurrence. For instance, there are many different predicted impacts on marine nitrogen cycling, with the potential to interface with marine primary productivity, depending on which nutrient is limiting over different time scales [88,89].

(*a*) *Large magnitude of industrial nitrogen fixation*

The industrial production of nitrogenous fertilizers through the Haber–Bosch process is now carried out on a vast scale [90]. Nitrogen-containing fertilizers are applied globally to arable farming land to stimulate crop yields. Following the invention of the process in the early 1900s, most of the nitrogen in these fertilizers is produced nowadays by converting some of the enormous atmospheric reservoir (more than 78% of all air is N_2) to ammonia, which is subsequently converted to solid nitrogen in fertilizers. The scale of this industrial N_2 fixation is very large, approximately $100\,\mathrm{Tg\,N\,yr^{-1}}$, and comparable to the amount of N_2 fixation that takes place naturally on land or in the ocean [91].

(*b*) *Nutrients and primary production*

These nitrogenous fertilizers are obviously applied to the land surface and not to the sea directly. Large quantities nevertheless end up in the sea, after following various routes. The most straightforward is through rain washing fertilizers off fields and into drainage channels and streams and rivers, which then transport the anthropogenic nitrogen eventually to the coastal ocean, where blooms are commonly seen near to river mouths or in restricted seas such as the Gulf of California [92]. Application of fertilizers (containing nitrogen but also phosphorus and other nutrients) to farmland thus leads indirectly to fuelling of algal production in coastal seas. When this extra algal biomass falls into, and then decays in, deeper water, this often leads to stripping out of all available oxygen, because aerobic decomposition uses up oxygen. Eutrophication, as this

phenomenon is known, therefore refers not only to high algal biomass but also to the consequent deoxygenated waters, such as have been observed for a number of years in the Gulf of Mexico. The seasonal 'dead zone' in the Gulf of Mexico is a consequence of increased nutrient delivery from the Mississippi [93]. It predates and is unconnected with the recent Deepwater Horizon oil spill.

Although nutrient-fuelled algal production necessarily sequesters carbon dioxide as it grows and then sinks to deeper waters, the effect is not quantitatively significant over centuries. For instance, it has been calculated [61], using a variety of models and supported by back-of-the-envelope calculations, that, between 2000 and 2100, the maximum likely effect is a drawdown of only $3\,\mu$atm CO_2. Clearly, however, the effect will accumulate over time and become increasingly significant if the elevated nutrient input rates can be sustained. While continued synthesis of nitrogen fertilizers is not a problem, because of the very large atmospheric reservoir, it may be more problematic for phosphorus, for instance, because of limited availability of deposits that can be mined.

There are additional routes by which human activities fertilize the oceans. Sewage stations release nitrogen, phosphorus and other nutrients. It has been shown that polluted forests downwind of industrial centres, such as the Hubbard Brook Experimental Forest in New Hampshire in the USA, release nitrogen to streams in much greater quantities than do unpolluted forests in the far south of South America [94]. The probable explanation is that air-borne nitrogen deposited on Hubbard Brook leads to trees there receiving a surfeit of nitrogen and for this reason not taking up nitrogen as actively as before from the soils in which they are growing. The net effect is, again, a greater amount of bioavailable nitrogen flowing into streams and rivers and thence to the sea.

Nitrogen is also directly transported to the ocean through the atmosphere in great quantities (approx. $50\,\text{Tg}\,\text{N}\,\text{yr}^{-1}$; [95]). It is calculated that direct atmospheric deposition of bioavailable N to the surface oceans is becoming increasingly important compared with natural supply such as through upwelling [95]. However, the importance of atmospheric deposition varies greatly with location, depending on prevailing winds and proximity to centres of industrial activity.

It can be expected that the increasing supply of bioavailable nitrogen to the oceans will tend to raise levels of bioavailable N somewhat, and thereby suppress naturally occurring N_2 fixation, opposing the overall rise in bioavailable N. It is not presently known, however, whether such a feedback is actually taking place. It has however been suggested that the future could see increasing N_2 fixation taking place in the oceans, potentially owing both to higher CO_2 (§3c) and to a greater supply of iron. The latter effect could occur through desertification and increased aridity in the Sahel (Africa) and elsewhere. As land-derived dust (containing iron) is blown out to sea, it provides a source of iron to surface waters remote from land, where scarcity of iron can be a limiting factor restraining N_2 fixation [96].

(c) Oxygen-minimum zones

Repeat measurements of oxygen concentrations over many years have revealed a decline in oxygen concentrations in subsurface waters (100–1000 m depth) at many locations around the world [97]. The decline is probably caused

by a combination of two factors: (i) decreased solubility of all gases in a warming surface ocean, leading to less oxygen in surface waters ([98] and references therein), and (ii) increased stratification (§2*d*), leading to less mixing of subsurface waters with higher oxygen surface waters. By combining historical databases with more recent measurements, it has been possible to construct 50 year long time series of dissolved oxygen concentrations. Lack of oxygen (below about 60–$120 \, \mu\mathrm{mol} \, \mathrm{kg}^{-1}$) is a problem for animals, because it is required for powering their metabolisms. In most locations, the ongoing oxygen decline is likely to have little effect because there is still plenty of oxygen left to satisfy the needs of organisms. In other locations, however, particularly those close to the Equator and towards the eastern edges of the different ocean basins, this decline is exacerbating an existing scarcity and is expanding the sizes of the oxygen-minimum zones [97,99]. Many animals are therefore excluded from these oxygen-poor waters. Biogeochemical processes that occur only in low-oxygen conditions, such as denitrification and anammox, are likely to become more important. Although oxygen-minimum zones are expanding, there is no suggestion that the ocean will come to resemble anything like that seen during OAEs in the past.

(*d*) *Dams and diatoms*

Although the general trend is for human impacts to increase the amounts of nutrients transported to the ocean in rivers, dissolved silicate (silicic acid) is probably an exception. The difference arises because of the widespread damming of rivers. It appears that dams do not greatly alter flows of nitrogen and phosphorus. For silicon, in contrast, diatoms bloom in considerable quantities in dam reservoirs, and it is suggested that the sedimentation of diatoms behind dams is stripping silicon from river water.

This supposition is supported by (i) data showing declining silicic acid concentrations over time in the Black Sea (into which the Danube flows) [100], (ii) data showing a 50 per cent decline in Mississippi silicate concentrations [101] and (iii) data showing declining silicate to nitrate ratios downstream of the Yangtze River Three Gorges Dam, following its completion in 2006 [102]. This supposition is not supported, however, puzzlingly, by measurements of silicic acid concentrations just above and just below the Iron Gates Dam on the Danube, which show only a small drop in silicate concentration across the dam [103].

The reduction in river-supplied silicate, while other nutrients are supplied at greater rates, is likely to lead to a floristic shift in the phytoplankton. Diatoms are likely to gradually become less numerous among the phytoplankton, firstly in enclosed and marginal seas, and then much more slowly (the residence time of silicate in the global ocean is of the order of 20 000 years) in the ocean as a whole.

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