Sensitivities of marine carbon fluxes to ocean change

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Throughout Earth's history, the oceans have played a dominant role in the climate system through the storage and transport of heat and the exchange of water and climate-relevant gases with the atmosphere. The ocean's heat capacity is ≈1,000 times larger than that of the atmosphere, its content of reactive carbon more than 60 times larger. Through a variety of physical, chemical, and biological processes, the ocean acts as a driver of climate variability on time scales ranging from seasonal to interannual to decadal to glacial–interglacial. The same processes will also be involved in future responses of the ocean to global change. Here we assess the responses of the seawater carbonate system and of the ocean's physical and biological carbon pumps to (*i*) ocean warming and the associated changes in vertical mixing and overturning circulation, and (*ii*) ocean acidification and carbonation. Our analysis underscores that many of these responses have the potential for significant feedback to the climate system. Because several of the underlying processes are interlinked and nonlinear, the sign and magnitude of the ocean's carbon cycle feedback to climate change is yet unknown. Understanding these processes and their sensitivities to global change will be crucial to our ability to project future climate change.

climate change | marine carbon cycle | ocean acidification | ocean warming

The ocean is presently undergoing major changes. Over the past 50 years, the ocean has stored 20 times more heat than the atmosphere (1). The Arctic Ocean surface layers have recently experienced a pronounced freshening (2), and although there is still considerable uncertainty in current observational estimates (3), climate models run under increasing atmospheric CO_2 levels essentially all predict a slowdown of the Atlantic meridional overturning circulation (MOC), which is part of the global thermohaline circulation (4). Since preindustrial times, the ocean has also taken up ≈50% of fossil fuel CO_2, which has already led to substantial changes in its chemical properties (5).

Carbon fluxes from the sea surface into the ocean interior are often described in terms of a solubility pump and a biological pump (6). The abiotic solubility pump is caused by the solubility of CO_2 increasing with decreasing temperature. In present climate conditions, deep water forms at high latitudes. As a result, volume-averaged ocean temperatures are lower than average sea-surface temperatures. The solubility pump then ensures that, associated with the mean vertical temperature gradient, there is a vertical gradient of dissolved inorganic carbon (DIC). This solubility-driven gradient explains ≈30–40% of today's ocean surface-to-depth DIC gradient (7).

A key process responsible for the remaining two thirds of the surface-to-depth DIC gradient is the biological carbon pump. It transports photosynthetically fixed organic carbon from the sunlit surface layer to the deep ocean. Integrated over the global ocean, the biotically mediated oceanic surface-to-depth DIC gradient corresponds to a carbon pool 3.5 times larger than the total amount of atmospheric carbon dioxide (8) and has a mean residence of a few hundred years. Hence, small changes in this pool, caused, for example, by biological responses to ocean change, would have a strong effect on atmospheric CO_2. Counteracting the organic carbon pump in terms of its effect on air–sea CO_2 exchange is a process termed the carbonate counter pump (9), also known as the alkalinity pump. The formation of $CaCO_3$ shell material by calcifying plankton and its sinking to depth lowers the DIC and alkalinity in the surface ocean, causing an increase in CO_2 partial pressure. It is worth noting that the organic and inorganic carbon pumps reinforce each other in terms of maintaining a vertical DIC gradient, whereas they are counteractive with respect to their impact on air–sea CO_2 exchange.

Although the range of potential changes in the solubility pump and chemical responses of the marine CO_2 system is known reasonably well, our understanding of biological responses to ocean change is still in its infancy. Such responses relate both to possible direct effects of rising atmospheric CO_2 through ocean acidification (decreasing seawater pH) and ocean carbonation (increasing CO_2 concentration), and indirect effects through ocean warming and changes in circulation and mixing regimes. These changes are expected to impact marine ecosystem structure and functioning and have the potential to alter the cycling of carbon and nutrients in the surface ocean with likely feedbacks on the climate system.

Changes in the Solubility Pump. Alterations in the physical state of the ocean will affect both the solubility pump and the biological pump. For finite-amplitude perturbations, changes in both pumps interact nonlinearly and therefore cannot be considered separately. For conceptual simplification, however, we will here focus on physical impacts on the solubility pump only before discussing impacts on the biological pump in a later section.

Rising atmospheric CO_2 leads to higher sea-surface temperature (SST) and a concurrent reduction in CO_2 solubility. It is estimated that this positive SST feedback will reduce the oceanic uptake of anthropogenic carbon by 9–15% [≈45–70 gigatons carbon (Gt C)] by the end of the 21st century (10–13). Global warming will also intensify the hydrological cycle. The direct dilution effect on CO_2 solubility is small compared with the temperature effect and is expected to largely cancel out at the global scale as enhanced precipitation in one area tends to be balanced by enhanced evaporation in another area. Overall, the expected effect of direct dilution on anthropogenic CO_2 uptake is of uncertain sign but estimated to be much smaller than 1% (13). A potentially more significant impact of changes in the hydrological cycle on the oceanic CO_2 uptake can arise at high latitudes in the North Atlantic: Here, reduced surface salinities, together with higher SSTs, would lower the density of surface waters and thereby may inhibit the formation of deep waters. This lowering in turn would reduce meridional pressure gradients and tend to slow down the thermohaline-driven part of the meridional, overturning circulation. Climate model simulations indeed predict a gen-

eral weakening of the North Atlantic MOC for the 21st century when forced with increasing greenhouse gas concentrations (4, 14). Complementary to the simulated weakening of the Atlantic MOC, climate models also predict an intensification of the ocean circulation in the Southern Ocean, resulting from a larger warming in mid and low latitudes compared with the waters around Antarctica. In consequence, the meridional pressure gradients are predicted to increase both across the Antarctic Circumpolar Current (15) and in the atmosphere above the Southern Ocean (16). Estimates of the total impact of the circulation changes on the solubility pump differ considerably among different models, predicting a reduction in global oceanic carbon uptake by some 3–20% (17). A major part of the large uncertainty can be attributed to our incomplete understanding of the Southern Ocean's role as a carbon sink.

Chemical Response of the Marine CO_2 System.

A significant portion of the carbon released by humankind in the Anthropocene era has been—and will continue to be—redistributed to the world ocean. The ocean owes its huge CO_2-uptake capacity to the presence of the carbonate ion (CO_3^{2-}), which can react with excess CO_2 taken up from the atmosphere according to the following net buffering reaction (Note that the two analytically indistinguishable species, CO_2 and H_2CO_3, are usually combined as hypothetical species CO_2^*.):

$$CO_2^* + CO_3^{2-} + H_2O \rightarrow 2HCO_3^- \quad [1]$$

The oceanic uptake capacity which amounts to nearly 85% (not including the buffering by sedimentary carbonates) of the entire anthropogenic carbon released to date (340–420 Gt C) (5), can only be accommodated, however, on the turnover time scale of the ocean, i.e., several centuries to millennia. The present oceanic uptake of ≈27% of the current anthropogenic carbon emissions (5) therefore falls markedly short of the thermodynamic uptake capacity. As the ocean continues to take up anthropogenic CO_2, significant speciation changes in the marine CO_2 system take place that lead to a progressive reduction of the buffering capacity. These changes will not only cause a decrease in the ocean's uptake ratio, i.e., the equilibrium change in DIC per change in atmospheric CO_2 concentration, but also lead to an amplification of the effects of thermal and biological forcing on the natural oceanic carbon cycle. These changes in the marine CO_2 system, which we will explore in the following, are inherently nonlinear and will amplify with time.
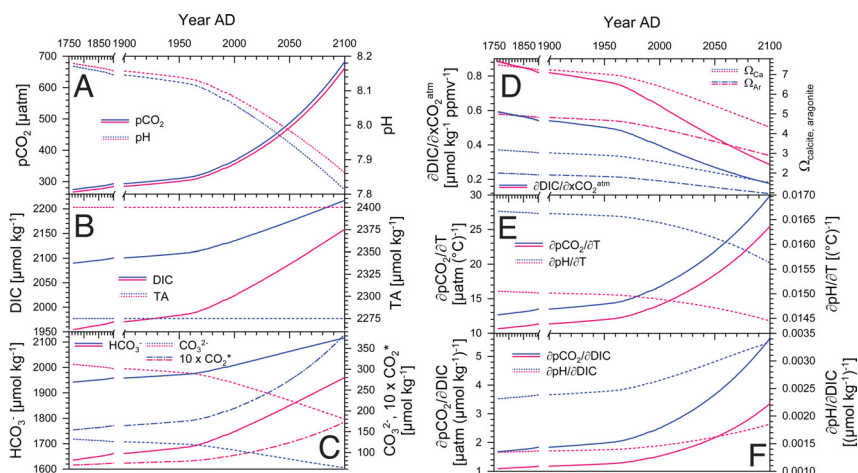

Fig. 1. Trends and projections of changes in the properties of the marine CO_2 system in cold (blue) and warm (red) surface waters between 1750 and 2100 under the prescribed atmospheric CO_2 increase. (*A*) Equilibrium CO_2 partial pressure (pCO_2) and pH. (*B*) Equilibrium DIC and TA. (*C*) Concentrations of the three species CO_2^*, HCO_3^-, and CO_3^{2-} (note that the concentration of CO_2^* is multiplied by a factor of 10. (*D*) CO_2-uptake ratio and saturation states (Ω) of calcite and aragonite. (*E*) Temperature sensitivities of pCO_2 and pH. (*F*) Chemical (i.e., CO_2) sensitivities of pCO_2 and pH. See *SI Text* for details on the calculation and assumptions made therein.

To illustrate changes in the properties of the marine CO_2 system during the course of the 21st century, we need to prescribe the development of atmospheric CO_2 concentrations. With vastly differing emission scenarios and a host of open questions, we opted for a rather simplistic approach in which we extrapolated recent growth rates to yield an atmospheric CO_2 concentration of almost 700 parts per million by volume (ppmv) by the end of the 21st century (see *SI Text* for details on the calculations and all assumptions involved). The oceanic response exerted by this atmospheric boundary condition will be regionally different depending mainly on seawater temperature and the general characteristics of the marine CO_2 system. To capture the entire sensitivity range, we define a cold- and warm-water case roughly representing polar and tropical surface waters. In both cases, changes in CO_2 system parameters pCO_2, pH, and DIC as well as concurrent changes in CO_2 system speciation (HCO_3^-, CO_3^{2-}, CO_2^*) were calculated (Fig. 1 *A–C*). These speciation shifts also affect other CO_2 system properties such as the CO_2 buffering capacity expressed by the uptake factor ($\delta DIC/\delta xCO_2^{atm}$), the saturation state with respect to the calcium carbonate minerals calcite and aragonite as well as the sensitivities of pCO_2 and pH to thermal and biologically mediated chemical forcing (Fig. 1 *D–E*).

As expected, surface-ocean DIC increases along with pCO_2 as a consequence of uptake of "excess" atmospheric CO_2 (Fig. 1*B*), a process known as "ocean carbonation." The concurrent drop in surface-ocean pH is a mirror image of the pCO_2 increase and amounts to 0.3–0.4 pH

units (Fig. 1*A*). This increase in the hydrogen ion (H^+) concentration of up to 250%, also referred to as "ocean acidification," is currently of growing concern among marine biologists. Also note that it is entirely unclear whether the corresponding decrease of the hydroxide ion concentration by up to 60% could also have consequences for chemical reactions or equilibria involving OH^- (e.g., solubility of iron hydroxides); this aspect warrants a closer look. According to Eq. **1**, the uptake of atmospheric CO_2 in addition to CO_2^* increases HCO_3^- at the expense of CO_3^{2-} (Fig. 1*C*). By converting one molecule of CO_3^{2-} to two molecules of HCO_3^- this reaction is neutral, however, for total alkalinity (18).

The marked drop in CO_3^{2-} has distinct effects on two important properties of the marine CO_2 system: First, the CO_2 uptake capacity, expressed as the equilibrium DIC increase per rise of atmospheric CO_2 ($\delta DIC/\delta xCO_2^{atm}$), is attenuated to less than a third of its preindustrial value. Hence, at equilibrium one liter of seawater in 2100 will sequester only one third of the atmospheric CO_2 (per ppmv increase) it sequestered in 1750 (Fig. 1*D*). This is a rather drastic change that must be (and usually is) taken into account in future projections. Secondly, the ubiquitous supersaturation of surface waters with respect to the calcium carbonate minerals calcite and aragonite falls to about a half (50–60%, Fig. 1*D*) of its preindustrial level. Thus, cold surface waters in high latitudes will be the first to no longer be supersaturated and may even turn corrosive to carbonate minerals (19, 20).

Beyond these prominent and well-documented effects, there are other

changes in the properties of the marine CO_2 system that do not appear to have received as much attention. These changes pertain to the inherent sensitivity of the CO_2 system to thermal and chemical forcing, most importantly the impacts of the seasonal cycle of SST and net biogenic production of particulate organic and inorganic carbon on the ocean's source/sink patterns for atmospheric CO_2. Large regions of the world ocean show marked SST seasonality, which directly affects the temperature-sensitive parameters pCO_2 and pH [but not the conservative properties DIC and total alkalinity (TA), if expressed in gravimetric units]. As the anthropogenic perturbation of the marine CO_2 system enhances the temperature sensitivity of pCO_2 ($\delta pCO_2/\delta T$) by almost a factor of 2.5 in our extrapolation (Fig. 1E), the effect of the natural seasonal SST forcing will be strongly amplified, leading to marked modulation of the seasonal air–sea CO_2 flux pattern. In contrast, seawater pH will only be marginally affected with even a slight reduction in the temperature sensitivity ($\delta pH/\delta T$).

The second major driver of natural seasonal variability in the surface-ocean carbon cycle are biologically driven chemical changes, i.e., withdrawal of carbon through net production of organic carbon as well as particulate carbonates (e.g., calcite and aragonite). The sensitivities of pCO_2 and pH with respect to organic carbon production, which to a first-order approximation affects DIC but not TA, are both amplified by the anthropogenic perturbation. The enhancement by a factor >3 by year 2100 for pCO_2 ($\delta pCO_2/\delta DIC$) is again much larger than for pH ($\delta pH/\delta DIC$), which will increase by a factor of only ≈1.4 (Fig. 1F). Overall, pCO_2 is thus affected most strongly by changes in physical and (biologically mediated) chemical forcing, which has implications for the seasonal CO_2 sink/source pattern. The seawater pH, in contrast, is much less affected.

The thermal and biochemical drivers of the natural seasonal CO_2 sink/source patterns of the ocean have been explored in detail (e.g., 21–24). Unlike for oxygen, the two have counteracting effects on pCO_2. In major parts of the world ocean, however, one factor dominates, and a clear seasonal pCO_2 cycle results. Especially in these regions, changing thermal and chemical sensitivities will give rise to an alteration of the seasonal cycle of pCO_2 with higher peak-to-peak amplitudes and potentially also a change in the sign of the disequilibrium. To make the superimposed effects of these counteracting processes more palpable, we illustrate the situation with a realistic example. We have chosen the Labrador Sea as a high-latitude example where the seasonal pCO_2

Fig. 2. Seasonal cycle of pCO_2 (A) and pH (B) anomalies at present (year 2004, continuous lines) and in the future (year 2100, dashed lines) at a location in the central Labrador Sea (56.5° N, 52.6° W). Also shown are pCO_2 observations (from 20) on which this analysis is based. See *SI Text* for details on the calculation and assumptions made therein.

cycle features a marked summer minimum (winter maximum) because of the dominance of biological over thermal forcing (Fig. 2A).

As shown by ref. 23, the observed annual pCO_2 cycle in the central Labrador Sea can be deconvoluted into a thermal (i.e., isochemical) and a chemical (i.e., isothermal) component, where most of the chemical effect is mediated by carbon uptake via net biological production. Assuming no change in the thermal and chemical forcing, hypothetical seasonal pCO_2 and pH cycles can be constructed for the year 2100 (Fig. 2). The increase in the peak-to-peak amplitudes is significant in both but much stronger in pCO_2. Note that although in year 2100 pH is lower and shows a larger seasonal amplitude than in 2004, saturation states of calcite and aragonite show a reduced seasonal amplitude even though they are also lower. At first sight, the pCO_2 effects may appear to be a mere intensification of the seasonal pCO_2 and hence CO_2 source/sink cycle with little net affect. In regions where on an annual average a disequilibrium is observed, however, a significant net effect may result. The Labrador Sea, for example, is nearly neutral in winter and a strong sink in summer (Fig. 3) with an overall annual CO_2 sink of 2.7 mol m^{-2} yr^{-1} in 2004 (23). In our extrapolation, the summer sink is enhanced

whereas the region turns into a CO_2 source in winter. If we further take into account the marked seasonality in wind speed, the physical driving force of air–sea exchange, it becomes obvious that strong net effects on the annual source/sink function can occur (Fig. 3). In our case, the overall net CO_2 sink in 2100 is projected to drop to about half the sink observed 2004.

The well-documented climatological CO_2 source/sink patterns of the present ocean (21, 22) are largely a consequence of the two big, natural, counteracting forces, both of which are enhanced as surface-ocean pCO_2 levels rise in concert with the atmospheric pCO_2. As shown above, the balance between the two responses—and hence the net ocean-source/-sink function for the atmospheric CO_2 budget—will be affected, even without the need to invoke any changes in the general physical and biological forcing of the marine carbon cycle. If we further include the possibility of such changes in the forcing itself, which may partly compensate and partly enhance the responses presented above, it becomes clear that the reduction in the buffering capacity of the ocean's CO_2 system is a critical system response with significant feedback potential.

Biotic Responses to Ocean Warming. Ocean warming impacts the pelagic ecosystem
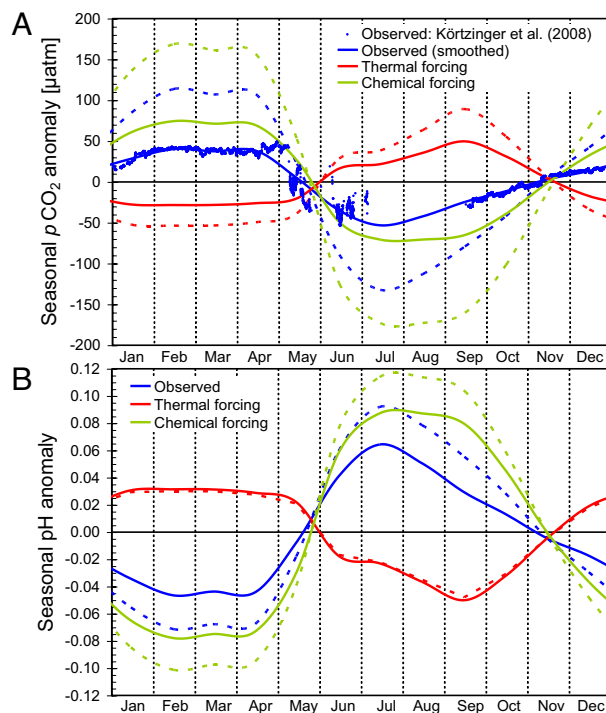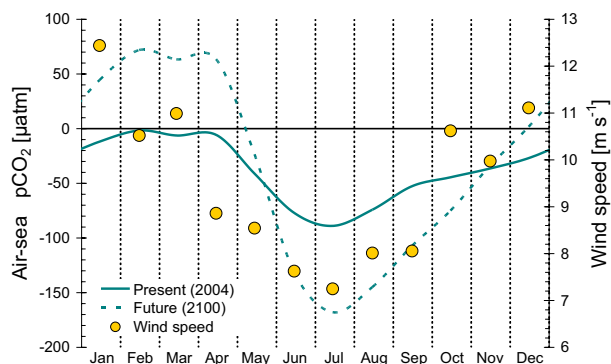
Fig. 3. Monthly mean air–sea disequilibrium at a location in the central Labrador Sea (56.5° N, 52.6° W) in years 2004 (continuous line) and 2100 (broken line). Also shown is monthly mean climatological wind speed at this location.

Fig. 4. Schematic model illustrating the effect of sea-surface warming on upper-ocean processes in low (*Upper*) and high (*Lower*) latitudes. Graph depicts effects on stratification and mixed-layer depths, nutrient supply (yellow arrows), plankton biomass, and particle flux (green arrows).

both directly and indirectly in three ways: (*i*) through decreased supply of plant nutrients because of a slowdown in vertical mixing and convective overturning; (*ii*) through increased thermal stratification, causing increasing light availability for photosynthetic organisms suspended in the upper mixed layer; and (*iii*) through the effect of increasing temperatures on the rates of biological processes. Which of these factors will dominate in a particular region and at a given time depends on the hydrographic conditions, the composition of the pelagic community, and the activities of its individual components.

Changes in Circulation and Mixing. A reduction in the overturning circulation can be expected to reduce the supply of nutrients to the surface waters. In areas in which surface nutrient concentrations are already zero, this reduction will not change surface nutrient concentrations and, for constant stoichiometry, surface DIC levels. Despite a possible reduction in biomass and its turnover, the first-order effect on air–sea CO_2 exchange will be small in these areas. Regions with non-zero surface nutrient concentrations, however, can experience declining surface nutrient and DIC concentrations for a slower circulation, which will allow more atmospheric CO_2 to enter the ocean. Without exchange with the underlying waters, utilization of the nutrients in the upper 50 m of the global ocean would correspond to a one-time additional carbon uptake of ≈ 8 Gt C. Subduction of the newly nutrient-depleted waters and replacement by nutrient-rich subsurface waters can, however, allow for a repeated uptake of atmospheric carbon. This process eventually leads to a reduction of preformed nutrients and a corresponding increase of regenerated nutrients and carbon below the surface layer at the expense of a decline in the atmospheric carbon pool (25). Particularly in the Southern Ocean, the dynamics of converting pre-

formed nutrients into regenerated nutrients will be modulated by the concomitant reduction in the supply of the often limiting micronutrient iron (26) under changing light conditions (27).

Increased thermal stratification due to rising SST affects both nutrient supply and mixed-layer light intensities. In the tropics and midlatitudes, where thermal stratification restricts vertical mixing, typically low surface nutrient concentrations limit phytoplankton growth. Ocean warming will further reduce mixing, diminishing the upward nutrient supply and lowering productivity (Fig. 4 *Upper*). At higher latitudes, phytoplankton is often light-limited because intense vertical mixing circulates algal cells over deep mixed layers, resulting in lower mean light intensity along a phytoplankton cell's trajectory and hence lower net productivity. In these regions, ocean warming and a greater influx of fresh water, mostly from increased precipitation and melting sea ice, will contribute to reduce vertical mixing which may increase productivity (Fig. 4 *Lower*).

Temperature Effects on Biological Activities. Direct biotic responses to increasing temperatures will differ greatly among the various components of the pelagic ecosystem, most notably between the autotrophic and heterotrophic communities. The temperature dependence of biological processes is commonly expressed by the Q_{10} factor—the factorial increase in the rate for a 10° C increase in temperature. Although bacterial heterotrophic activities typically have a Q_{10} factor between 2 and 3 (28), phytoplankton growth and photosynthesis show only a moderate temperature sensitivity ($1 < Q_{10} < 2$) (29) and are primarily controlled by incident light intensity. Bacterial growth efficiency, on the other hand, is an inverse function of temperature, causing an increased fraction of the assimilated carbon to be respired with rising temperature (30). These diverging temperature sensitivities will likely induce
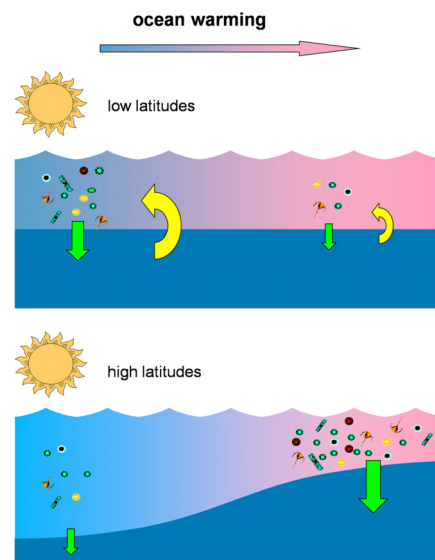
a complex nonlinear response to ocean warming at the community and ecosystem levels. Although shoaling of the upper mixed layer primarily affects the autotrophic community through increased light intensities in this layer, increasing seawater temperature mainly affects the activity of the heterotrophic community. The net outcome depends on the balance of light and temperature sensitivities and dynamic interaction of the different groups of auto- and heterotrophic organisms and cannot be easily deduced from physiology-based first principles.

A number of different approaches consistently predict an overall decrease in primary and export production in the tropics and midlatitudes and a pole-ward migration of geographic boundaries separating biogeochemical provinces:

(*i*) coupled atmosphere ocean general circulation models (AOGCMs) combined with mechanistic models of pelagic ecosystems that directly predict biological responses (e.g., 31–33);

(*ii*) climate response patterns in the AOGCMs that are similar to observed modes of interannual variability such as the El Niño/Southern Oscillation or Pacific Decadal Oscillation (34, 35); and

(*iii*) empirical models based on observational estimates of physical controls on current distributions of chlorophyll and primary production (36).

Biotic Responses to Ocean Acidification (OA). Oceanic uptake of anthropogenic CO_2 and the resulting changes in seawater chemistry will, in the course of this cen-

tury, expose marine organisms to conditions which they may not have experienced during their recent evolutionary history (37). The impact these changes will have on marine life is still uncertain, but there are likely to be both winners and losers. In fact, with regard to the potential biological effects of oceanic CO_2 uptake, the term "ocean acidification" only encompasses one side of the story. Although the decrease in seawater pH may pose a threat to the fitness of pH-sensitive groups, in particular calcifying organisms, "ocean carbonation"—the increasing oceanic CO_2 concentration—will likely be beneficial to some groups of photosynthetic organisms, particularly those that operate a relatively inefficient CO_2 acquisition pathway.

Adverse effects of ocean acidification are expected on various groups of calcifying organisms, including corals, bivalves, gastropods, and sea urchins, and possibly on the many other groups that use $CaCO_3$ as internal or external structural elements, such as crustaceans, cnidaria, sponges, bryozoa, annelids, brachiopods, tunicates, squid, and fish (38). The loss of competitive fitness in these groups may lead to the loss of biodiversity and the restructuring of marine ecosystems. To what extent such changes would affect marine productivity, transfer of energy through the food web, or biogeochemical cycling is presently unknown. Of relevance to the carbonate pump are the pelagic calcifying groups, in particular the coccolithophores, foraminifera, and pteropods. Most studies to date indicate a decrease in calcification of these groups with increasing seawater acidification, both in laboratory experiments (e.g., 39–42) and field studies (43, 44). However, this point remains controversial (45, 46).

Stimulating effects of ocean carbonation have been primarily observed for processes related to photosynthetic activity. These effects include CO_2-enhanced rates of phytoplankton growth and carbon fixation (47, 48), organic matter production (49, 50), and extracellular organic matter production (51). CO_2 sensitivity of autotrophic processes is also evident from changes in the cellular carbon:nitrogen: phosphorus (C:N:P) ratios of marine microalgae with CO_2 concentration (52). A shift in the ratio of carbon to nutrient drawdown toward higher C:N and C:P at elevated pCO_2 was observed during a mesocosm study in a natural plankton community (53). Recent studies with the diazotrophic cyanobacterium *Trichodesmium* revealed an increase in both carbon and nitrogen fixation with increasing pCO_2 (54–56). As primary producers in the marine realm encompass very phylogenetically diverse groups of organisms (57) that differ widely in their photosynthetic appa-

Table 1. Biotic responses to sea surface warming and ocean carbonation/acidification and their feedback potential to the climate system

Feedback process	Sign of feedback	Sensitivity	Capacity	Longevity
Responses to ocean warming				
Nutrient supply to oligotrophic ocean		+++	±0	++
Nutrient supply to HNLC areas	negative	++	++	+++
Nutrient utilization efficiency	negative	++	++	+++
Nutrient inventory	positive		++	+++
Organic matter remineralisation	positive			
Responses to ocean acidification				
Calcification	negative	+[†]	+	+[‡]
Ballast effect	positive		+++	+++
Stoichiometry	negative	++[†]	++	++
Extracellular organic matter production	negative	++[†]	+++	‡
Nitrogen fixation	negative	++[†]	+	‡

Responses are characterized with regard to feedback sign, sensitivity, capacity, and longevity by using best guesses; we use ±0 for negligible, + for low, ++ for moderate, and +++ for high. Empty boxes indicate missing information/ understanding.
[†]Available information mainly based on short-term perturbation experiments.
[‡]Potential for adaptation presently unknown. HNLC, high nutrient, low chlorophyll.

ratus and carbon-enrichment systems (58), it is presently difficult to assess which of these responses are specific to individual taxa or represent general phenomena across phytoplankton taxa or within functional groups.

Uncertainties. It is important to note that our present knowledge of pH/CO_2 sensitivities of marine organisms is based almost entirely on short-term perturbation experiments, neglecting the possibility of evolutionary adaptation. Also, little is presently known regarding the effects from multiple and interacting stressors, such as sea-surface warming and eutrophication. Moreover, there is a complete lack of information on the transfer of responses from the organism to the community and ecosystem levels and the replacement of OA-sensitive by OA-tolerant species.

Impacts on the Biological Carbon Pumps. For a comparison of the different biological responses to ocean change and their potential feedback to the climate system, we will apply four criteria to characterize each of the processes:

(*i*) the sign of the feedback, denoting whether a feedback amplifies (positive feedback) or dampens (negative feedback) the initial forcing;

(*ii*) the sensitivity, indicating the change needed to trigger the response;

(*iii*) the capacity, representing the feedback strength relative to the forcing and relative to other feedback mechanisms; and

(*iv*) the longevity, referring to the length of time a feedback may operate (i.e., transient versus long-lasting).

In categories *ii*, *iii*, and *iv*, we use ± 0 for negligible, + for low, ++ for moderate, and +++ for high values (Table 1). We wish to stress that our present under-

standing of biologically driven feedback mechanisms is still rudimentary, so the assigned values mostly represent best guesses. In some cases, we feel that our understanding is too immature to even make a guess.

Responses to Ocean Warming and Circulation. The effects of sea-surface warming on the marine biota and the resulting impacts on marine carbon cycling will differ depending on the prevailing light and nutrient conditions in the upper mixed layer and the composition of the pelagic community.

· Decreased nutrient supply to already-nutrient-limited areas of the ocean's surface layer is certain to lead to diminished primary production (sensitivity +++) and to a decline in the strength of the biological pump, i.e., the amount of biogenic carbon transported to depth. On the other hand, as nutrient supply to the surface layer slows down, so does the supply of dissolved inorganic carbon, slowing down the rate at which deep ocean CO_2 is brought back into contact with the atmosphere. Because the change in preformed nutrients is negligible in nutrient-limited areas, the overall effect on carbon sequestration can be expected to be negligible (capacity ±0) unless there is a change in C:N ratios in export production.

· Decreased nutrient supply to nutrient-replete (e.g., high-nutrient, low-chlorophyll) areas, may lead to lower levels in surface nutrients and DIC and in consequence reduce the total amount of preformed nutrients. Associated with these changes is an increase in regenerated nutrients and carbon in the ocean interior (sensitivity ++), resulting in a negative feedback of moderate capacity (++), which can last for several hundred years as long

as the supply of old preformed nutrients to the surface ocean from below exceeds the subduction of new preformed nutrients (longevity +++).

· Increased nutrient-utilization efficiency in the high latitudes, on the other hand, has a potentially strong effect on the efficiency of the biological pump (36) (capacity ++). With the shoaling of mixed-layer depths, currently nonused inorganic nutrients in high-latitude surface waters can be combined with CO_2 to form organic matter and be transported to depth (negative feedback). This change in efficiency affects the partitioning of the nutrient pool between preformed and regenerated nutrients and the associated partitioning of carbon among the atmospheric and oceanic carbon reservoirs (25). In the deeply mixed high-latitude areas of the northern North Atlantic and Southern Ocean, a significant shoaling of the mixed-layer depth is required to have a noticeable effect on nutrient utilization efficiency (sensitivity ++). Enhanced surface layer stratification in midlatitudes may also speed up the biomass accumulation during seasons of high productivity, e.g., during spring-bloom development, possibly affecting particle aggregation and sinking and the depth of remineralization. Provided that preformed nutrients continue to be supplied to the surface layer, this feedback could last for several hundred years (longevity +++).

· As sea-surface warming reduces deep-ocean ventilation, this slowdown will lower the supply of oxygen to the ocean interior (59). This process, which has been termed "ocean deoxygenation" (60), is expected to cause an overall decrease in deep-ocean oxygen content, including an expansion of oxygen-minimum zones (61, 62). Suboxic and anoxic conditions favor processes such as denitrification and anaerobic ammonium oxidation, leading to the loss of bioavailable nitrogen in the ocean, with possible implications for marine primary production. Provided that the ocean's nitrogen inventory ultimately determines the amount of carbon biologically sequestered in the ocean, reducing the nitrogen inventory would provide a positive feedback to the climate system. Suboxic conditions at the seafloor, on the other hand, favor the release of phosphate from sedimentary iron phosphates, possibly increasing the ocean's content of bioavailable phosphorus. A shift in the ocean's nitrate-to-phosphate content could affect the composition and productivity of marine primary producers. Most notably, the extra phosphate may be used by diazotrophic cyanobacteria, possibly counterbalancing the nitrogen loss from denitrification by nitrogen fixation. The net outcome of these complex interactions is difficult to assess, as is the sensitivity to ocean warming. (Capacity ++, longevity +++.)

· Although sea-surface warming directly affects all biological rates, the higher temperature sensitivity of heterotrophic (relative to autotrophic) processes is expected to shift the balance between primary production and respiration/remineralization in favor of the latter (63). Additionally, warming shifted the partitioning of organic carbon between the particulate and dissolved phase toward an enhanced accumulation of dissolved organic carbon (63). This shift may cause a decrease in the vertical flux of particulate organic matter and a decrease in remineralization depth. The overall effect could be a decline in the strength and efficiency of the carbon pump (positive feedback). Because of the complexity of plankton trophic interactions it is difficult, however, to assess the sensitivity and capacity of this feedback. Also unknown is the extent to which changes in community composition may compensate for the shifting balance between auto- and heterotrophic processes, making it impossible to make a judgement on the longevity of this feedback.

Ocean Acidification/Carbonation. Our understanding of the biological responses to CO_2-induced changes in seawater carbonate is still in its infancy. As research on ocean acidification gains momentum, new, unforeseen pH/CO_2 sensitivities emerge, with partly opposing impacts on carbon sequestration in the ocean.

· Decreased pelagic calcification and the resulting decline in the strength of the carbonate pump lower the drawdown of alkalinity in the surface layer, thereby increasing the uptake capacity for atmospheric CO_2 in the surface layer. Assuming an annual rate of $CaCO_3$ export of ≈1 Gt C (64), the capacity of this negative feedback is relatively small (65–68) (capacity +). The sensitivity of this response in coccolithophores appears to be highly species-dependent (69), permitting changes in species composition to dampen or eliminate the response at the community level (sensitivity +). Shifting species composition and the potential for adaptation (presently unknown) could make this a transient feedback (longevity +). In view of the scarcity of information on pH sensitivities of foraminifera and pteropods, however, it is premature to speculate on the significance of this feedback process.

· $CaCO_3$ may act as ballast in particle aggregates, accelerating the flux of particulate material to depth (70, 71; but see also ref. 72). Reduced $CaCO_3$ production could therefore slow down the vertical flux of biogenic matter to depth, shoaling the remineralization depth of organic carbon and decreasing carbon sequestration (65) (positive feedback). The capacity of this feedback depends on the pH sensitivity of pelagic calcifiers and the quantitative importance of $CaCO_3$ as ballast for particle export, both of which are poorly understood. If $CaCO_3$ turns out to be a prerequisite for deep transport of particulate organic matter, and if calcification of pelagic calcifiers remains sensitive to high CO_2, this feedback could have a potentially high capacity (+++) and extended duration (+++).

· A negative feedback also arises with increasing C:N drawdown, as observed in response to CO_2 enrichment in a mesocosm experiment (53). The capacity for this process depends on the relative increase in carbon consumption in excess of the Redfield ratio, which based on the observed 27% increase in response to a doubling in present day CO_2 can be considered moderate to high (capacity ++). It is not presently known whether the response observed for the mesocosm phytoplankton community, which was dominated by diatoms (mostly *Skeletonema* sp. and *Nitzschia* spp.) and the coccolithophore *Emiliania huxleyi*, also applies to other phytoplankton taxa and functional groups, or whether this response may be modified or lost because of adaptation to high CO_2. Hence, it appears too early to make a judgement on the sensitivity and longevity of this feedback. If there is a significant enhancement in the C:N drawdown at the surface that translates into an enhanced carbon export, it will lead to higher oxygen consumption and a possible expansion of oxygen-minimum zones (73), linking to the oxygen-related feedback described in *Responses to Ocean Warming and Acidification*.

· Increased production of extracellular organic matter under high CO_2 levels (51) may enhance the formation of particle aggregates (74, 75) and thereby increase the vertical flux of organic matter (negative feedback) (76). This response may in fact have been responsible for the observed increased in C:N:P stoichiometry observed at elevated pCO$_2$ (53, 77). Provided that the response is of general nature in bloom-forming phytoplankton (presently unknown sensitivity), the capacity of this process may be high because, similar to the ballast effect, it could lead to an increase in remineralization depth (capacity +++). Again, not knowing whether evolutionary adaptation will select against this response prevents a judgement on the longevity of this process.

· Enhanced nitrogen fixation at elevated pCO$_2$, as recently reported for the diazotrophic cyanobacterium *Trichodesmium* (54–56), has the potential to in-

crease the reservoir of bioavailable nitrogen in the surface layer, which in a predominantly nitrogen-limited ocean would increase primary production and carbon fixation (negative feedback). Because cyanobacteria-produced biomass is generally thought to not be exported to great depth, uncertainty exists about the extent to which the additional bioavailable nitrogen would lead to enhanced carbon sequestration or whether it would remain suspended in the surface layer, eventually eliminating the ecological niche for nitrogen-fixing cyanobacteria. As CO_2 sensitivity of nitrogen fixation has thus far been reported for only one species, it is too early to speculate about the sensitivity and longevity of this response.

Tipping Points. Although several of the cause-and-effect relationships described above have the potential to drastically alter the ocean's ecosystems and biogeochemistry, it is yet unclear if any of the predicted changes may turn out irreversible or may develop into runaway biogeochemical feedbacks. In the following, we will give four examples wherein sensitivities of ecological and biogeochemical processes to ocean change may develop into tipping points, possibly driving the ocean to a new state.

(*i*) A decrease of nutrient supply to the surface layer because of sea-surface warming in presently productive areas of the ocean may stimulate a dominance shift in the phytoplankton community from large diatoms to small-celled flagellates and cyanobacteria. A shift to smaller-celled phytoplankton causes an extension of the marine food web by one or more trophic levels (78). With 90% of the biomass and energy lost from one trophic level to the next, this shift would drastically reduce the efficiency of energy transfer from the level of primary producers to the top predators. Accelerating heterotrophic over autotrophic processes in a warming ocean will further reduce the transfer efficiency of primary-produced organic matter up the food chain. Moreover, as the growth efficiency of bacteria is an inverse function of temperature, a larger fraction of assimilated carbon is respired at elevated temperatures (30, 63). As these responses all contribute to accelerating the spinning of the wheel at the lower trophic levels, a warmer and more stratified ocean may shift into a new and lower state of energy-transfer efficiency, involving reduced fish production.

(*ii*) Depending on the still incompletely understood role of $CaCO_3$ as mineral ballast for organic carbon export, ocean acidification might, via a reduction in $CaCO_3$ formation, lead to a substantial decrease of the efficiency of the biological pump. This decrease would lead to a change in upper-ocean nutrient and oxygen status (68) with likely impacts on the pelagic community structure. The reduction in export would also present a strong positive feedback on atmospheric CO_2 (68) and, in turn, on ocean acidification (65). However, the postulated increase in the production of extracellular organic carbon under high CO_2 levels may partly compensate for the loss of $CaCO_3$ ballast by favoring aggregation of organic matter and non-$CaCO_3$ minerals (72). Given the current state of our knowledge, the efficiency of the biological pump could change significantly in either the positive or negative direction.

(*iii*) With regard to ocean acidification, a distinct tipping point may arise when seawater turns undersaturated with respect to calcium carbonate and becomes corrosive for the shells and skeletons of calcifying organisms. In the Southern Ocean, for example, wintertime undersaturation for aragonite is projected to occur at CO_2 levels of 450 ppmv, which under business-as-usual (Intergovernmenal Panel on Climate Change IS92a scenario) CO_2 emissions will occur by 2030 and no later than 2038 (79). Wintertime saturation states are of particular relevance to one of the key species of polar ecosystems, the aragonite-producing pteropod *Limacina helicina*. As this species undergoes its larval development primarily during winter months, it may experience corrosive seawater conditions at a particularly sensitive phase of its life cycle within the next couple of decades. As *Limacina* is an important component in polar ocean food webs, linking lower levels of the food web to the top predators, its disappearance could mark the disruption of polar pelagic ecosystems.

(*iv*) For coral reef ecosystems, a tipping point will be reached when reef erosion exceeds reef accretion. At CO_2 levels of 560 ppmv, calcification of tropical corals is expected to decline by 30% (80, 81). At this stage, loss of coral structure in areas of high erosion may outpace coral calcification, in which case reefs will no longer be sustainable. As the carbonate saturation horizon—the depth below which calcium carbonate dissolves—shallows because of ocean acidification, cold-water corals become exposed to corrosive waters. These slow-growing corals, which inhabit cold waters down to 3,000-m water depth, have built extensive reef systems on the shelves and along the continental margins extending from Northern Norway to the west coast of Africa. With unabated

CO_2 emissions, 70% of the presently known reef locations will be in corrosive waters by the end of this century (82). Coral reefs provide the habitat for the ocean's most diverse ecosystems, are the breeding grounds for commercially important fish, protect shorelines in tropical areas from erosion and flooding, and generate billions of dollars annually in tourism.

Summary. The global carbon cycle is both driven by and a driver of Earth's climate system. In this system, climate change therefore goes hand in hand with a change in carbon cycling and a redistribution of reactive carbon among the carbon reservoirs in the atmosphere, terrestrial biosphere, and ocean. The distribution of carbon between these reservoirs is the result of a multitude of interconnected physical, chemical, and biological processes, many of which are sensitive to climate change themselves. A major challenge in Earth system science is determining which of these processes act as primary drivers in the natural climate cycle and how they interact in controlling carbon fluxes between the reservoirs.

The same challenge applies when trying to forecast the system's response to major perturbations of the carbon cycle, such as the release of CO_2 from fossil-fuel burning and land-use changes. At first sight, the ocean's role in this system appears to be that of a giant buffer, sequestering enormous amounts of CO_2 and thereby dampening CO_2-induced climate change. A closer look reveals that both the changing climate and the extra load of CO_2 sequestered by the ocean alter the oceanic carbon cycle to the extent of modifying its capacity for further uptake of anthropogenic CO_2. The net outcome of these modifications is still uncertain, largely due to our limited understanding of the underlying mechanisms. This uncertainty holds true particularly for those processes involving biologically mediated components, which because of the complexity and plasticity of biotic responses and interactions are extremely difficult to untangle. Progress in our understanding of these interacting processes and their sensitivities to ocean change requires the concerted effort of all relevant disciplines, from molecular and ecosystem biology, marine and atmospheric chemistry, physical oceanography and palaeoceanography, to atmosphere–ocean- and Earth-system modeling, and with close interactions between observationalists, experimentalists, and modelers.

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