Abstract

The concentration of atmospheric CO₂ is increasing due to emissions from burning of fossil fuels and changes in land use. Part of this “anthropogenic CO₂” invades the oceans causing a decrease of seawater pH; this process is called “ocean acidification.” The lowered pH, but also the concomitant changes in other properties of the carbonate system, affects marine life and the cycling of carbon in the ocean.

Keywords

Anthropogenic CO₂ • Seawater acidity • Saturation state • Climate change • Physical carbon pump • Global warming • Biological carbon pumps • Phytoplankton • Primary production • Calcification
Atmospheric CO₂

Atmospheric CO₂, measured as partial pressure (pCO₂) in units of micro-atmosphere (μatm), remained almost constant at about 280 μatm from the year 1000 until the beginning of the industrial revolution at the end of the eighteenth century. Since then, pCO₂ is rising and approached values more than 40% higher than preindustrial. CO₂ emissions are still increasing (currently >9 Pg C yr⁻¹; Peters et al. 2012), and thus one has to expect pCO₂ two to three times the preindustrial value for the end of this century (560–880 μatm according to scenario B2 and A1F1; Nakicenovic et al. 2000).

Air-Sea CO₂ Exchange and Ocean Carbonate Chemistry

The surface ocean exchanges gases with the atmosphere. Net CO₂ fluxes between air and water are driven by differences in pCO₂ of the atmosphere and the equilibrium pCO₂ of seawater at a given chemical composition and temperature; at equilibrium, these two partial pressures equal each other. Starting from an equilibrium state, an increase of atmospheric CO₂ would lead to invasion of CO₂ into the ocean. In contrast to other gases like oxygen or nitrogen, CO₂ not just dissolves in seawater: it reacts with water to form true carbonic acid (H₂CO₃) that largely dissociates to bicarbonate (HCO₃⁻) and hydrogen ions (H⁺). CO₂ can also react with carbonate ions (CO₃²⁻) to form HCO₃⁻ and H⁺. In both cases, the production of H⁺ results in an increase of the H⁺ concentration ([H⁺]) and thus to a decrease of pH, which is the negative logarithm of the H⁺ concentration (i.e., pH = −log₁₀[H⁺]).

The change in [H⁺] influences the weak (not fully dissociated) acid–base systems in seawater, and thus the change in pH is smaller than expected from the simple stoichiometry of “one H⁺ per CO₂ molecule added”. This buffering is due to high values of total alkalinity in seawater (TA = [HCO₃⁻] + 2 [CO₃²⁻] + [B(OH)₄⁻] ± minor components). Low-TA freshwater can take up much less CO₂ and experiences large pH decrease even at small inputs of acid. For more details of the marine carbonate system, compare, for example, Zeebe and Wolf-Gladrow (2001).

Rate of Surface Ocean Acidification and Regional Differences

The ocean currently takes up about one quarter of the anthropogenic CO₂ emissions, causing surface ocean concentrations of CO₂ and HCO₃⁻ to increase while CO₃²⁻ and pH decrease (Fig. 13.1). The term “ocean acidification” summarizes the above-described changes in the carbonate system, yet it is mostly used referring to the decrease in pH and [CO₃²⁻]. The term “carbonation,” on the other hand, relates to overall increase in dissolved inorganic carbon (DIC), in particular [CO₂].

Assuming an atmospheric pCO₂ of 750 μatm for the end of this century (IS92a scenario, Nakicenovic et al. 2000), surface ocean [CO₂] will have almost tripled relative to preindustrial concentrations. Concomitantly, [CO₃²⁻] and pH will have
dropped by 50% and 0.4 units, respectively. It should be noted that this drop in pH corresponds to an increase of 150% in the $\text{H}^+$ concentration. Such a rate of acidification is many times faster than whatever occurred over the last 55 Mio years (Hönisch et al. 2012).

Even though trends can be generalized for all oceans, different regions are differently affected by increasing $\text{pCO}_2$. Polar waters, for instance, are most strongly affected by ocean acidification due to the higher solubility of $\text{CO}_2$ in cold seawater. In the Arctic, the effect of freshening by rivers and sea ice melting (due to warming) intensifies the phenomenon even further because also TA is reduced in response to the higher freshwater input (Yamamoto-Kawai et al. 2009); hence the system is less buffered towards $\text{pCO}_2$-induced pH changes. Upwelling systems, on the other hand, already today have pH values as low as those predicted for the end of this century (Feely et al. 2008). These examples, however, also illustrate that the present-day spatial variation in the carbonate chemistry is as high as the predicted changes in response to a doubling of atmospheric $\text{pCO}_2$.

**The Physical Carbon Pump and Climate Change**

Because of the fast changes in atmospheric $\text{CO}_2$ concentrations, currently ocean acidification is primarily an upper ocean phenomenon. However, ocean
circulation and mixing transfer the acidification signal also into intermediate layers and finally the deep ocean. This is due to the so-called “physical” or “solubility” carbon pump: the solubility of CO₂ in seawater close to the freezing point is twice as high as in tropical surface water, and thus cold water contains large amounts of DIC. This cold, DIC-rich water sinks or is subducted in polar and subpolar regions filling the deep and intermediate ocean, by far the largest active carbon reservoir containing about 50 times more carbon than the atmosphere. The future uptake and storage of anthropogenic CO₂ by the physical carbon pump can be estimated using mathematical models taking into account ocean circulation and physicochemical properties of seawater. A source of uncertainty is, however, current and future climate change including variations in ocean forcing due to wind stress, freshwater, and heat fluxes, all of which impact on the strength of the physical carbon pump (Le Quéré et al. 2007).

Impact of Ocean Acidification on Marine Organisms and Ecosystems

While there is a high certainty about reasons and trends of ocean acidification, uncertainties remain with respect to many biological processes and the question, which organisms will belong to the losers and winners in future ecosystems.

For marine primary producers, the increased availability of DIC may potentially be beneficial and a number of studies have indeed observed increased photosynthetic carbon fixation under elevated pCO₂ (e.g., Tortell et al. 2008). Such “CO₂ fertilization” effects have been attributed to increased diffusive CO₂ supply for photosynthesis and/or reduced costs associated with active carbon acquisition (e.g., Kranz et al. 2010). Ocean acidification effects on primary production and growth are, however, strongly modulated by other environmental conditions (e.g., irradiance, nutrients) and cannot be generalized. While certain groups like cyanobacteria or sea grass appear to benefit strongly, the responses in diatoms, for instance, seem to be relatively small. In natural diatom-dominated assemblages, ocean acidification nonetheless induced pronounced species shifts (Tortell et al. 2008), illustrating that even small CO₂-dependent changes in growth and primary production can have large ecological consequences.

For calcifying organisms, by now there is good evidence that corals, gastropods, or coccolithophores (calcifying microalgae) will suffer from ocean acidification (Kroeker et al. 2010). Lowered calcification rates were attributed to the decrease in pH (and the concomitant higher costs of internal pH regulation), or they were related to [CO₃²⁻], which sets the saturation state (Ω) for carbonate minerals. Under present-day conditions, most surface waters are oversaturated with respect to calcite or aragonite and hence biogenic precipitation of these minerals is thermodynamically favored. With ocean acidification, however, the degree of saturation of surface waters is decreasing and polar waters, for instance, will become undersaturated within this century (Orr et al. 2005). This means not only that the production is less favored but also that skeletons are prone to dissolution.
The higher corrosiveness of seawater may also explain why the bioerosion of coral reefs is accelerated under ocean acidification (Wisshak et al. 2012). Overall, it is very likely that lowered calcification in response to ocean acidification affects the competitive abilities of calcifiers. In line with this, the number of calcifying organisms was found to be significantly lower at volcanic CO2 vents compared to the nonacidified surrounding (Hall-Spencer et al. 2008).

Fish and non-calcifying invertebrates also respond to ocean acidification, even though their sensitivity is generally much smaller than in calcifiers or primary producers. The higher tolerance to ocean acidification could be attributed to the fact that heterotrophic organisms exhibit a steep outward-directed CO2 gradient due to respiration; hence their acid–base regulation is used to deal with high CO2 conditions. Nonetheless, ocean acidification was shown to narrow down the aerobic scope of many animals, possibly due to higher costs involved in acid–base regulation and limitations in respiratory system to supply sufficient oxygen (Pörtner and Farrell 2008). As a consequence of this, the tolerance towards high temperatures is decreased under ocean acidification. This is especially troublesome for polar species as warming will be more severe than in other areas, and the organisms cannot refuge to colder regions. It also appears that juveniles and larval stages, which typically have a lower capacity for acid–base regulation, are more prone to ocean acidification than adults.

As illustrated, ocean acidification was shown to impact organisms from different trophic levels with potentially large consequences for the marine ecosystem as well as carbon cycling. For more details of biological impacts compare, for example, Gattuso and Hansson (2011).

The Biological Carbon Pump and Climate Change

In addition to the physical carbon pump, two biological carbon pumps impact on the marine carbon cycling. Particulate organic carbon (POC) is produced by marine microalgae and transformed by a complex food web. Part of this POC sinks out of the upper ocean into deeper layers or even down to the ocean floor. Most of the organic material, however, is remineralized in the water column or at the ocean bottom, leading to an increase of DIC in the respective depths. The sum of these processes is called the “soft tissue pump” or “organic carbon pump”. In addition to POC, calcium carbonate precipitated mainly by coccolithophores and foraminifera is exported from the upper ocean; it is either archived in sediments, especially at low water depths, or dissolved in the deep ocean. The sum of these processes is called the “calcium carbonate pump.”

Both biological carbon pumps contribute strongly to a vertical DIC gradient, and without the biological carbon pumps, preindustrial atmospheric pCO2 would have been about twice as high (Maier-Reimer et al. 1996). Given the importance of the biological pumps for atmospheric pCO2, one would like to know how its functioning may change in a future ocean. The three main stressors for marine organisms and ecosystems are ocean warming, ocean acidification, and
deoxygenation (Gruber 2011). Some of the resulting effects are changes in nutrient supply by circulation and mixing, changes in light regime by stronger stratification, changes in calcification and primary production due to ocean acidification or carbonation, responses of animals due to altered fitness, or changes in amount and quality of food in a warmer and acidified surface ocean. They all have impacts on ecosystem structure and functioning and hence likely also alter the strength of the biological pumps. However, owing to the complex and mostly unknown interplay of stressors on the various processes (Fig. 13.2), a conclusive answer about magnitude and direction of change cannot be provided at this moment.

**Take-Home Message**

Because of the fast increase of atmospheric CO₂ and slow mixing of ocean waters, ocean acidification is first of all an ocean surface phenomenon. Effects of ocean acidification, e.g., undersaturation for aragonite, will occur first in polar waters,
especially in the Arctic Ocean where low temperatures combine with freshening of surface waters. The physical carbon pump transports the acidification signal into deeper layers and is responsible for most of the uptake and storage of anthropogenic CO₂. Climate change has a measureable impact on the physical carbon pumping. The biological carbon pumps are of central importance for the oceanic carbon cycling. Marine organisms show various responses to ocean acidification. Because of the complexity of the biological pumps, their responses to climate change and ocean acidification are thus far difficult to predict.

References


Gruber N (2011) Warming up, turning sour, losing breath: ocean biogeochemistry under global change. Phil Trans R Soc A 369:1980–1996


