

Dieter A. Wolf-Gladrow and Björn Rost

## Contents

Atmospheric CO <sub>2</sub> .....	104
Air-Sea CO <sub>2</sub> Exchange and Ocean Carbonate Chemistry .....	104
Rate of Surface Ocean Acidification and Regional Differences .....	104
The Physical Carbon Pump and Climate Change .....	105
Impact of Ocean Acidification on Marine Organisms and Ecosystems .....	106
The Biological Carbon Pump and Climate Change .....	107
Take-Home Message .....	108
References .....	109

---

## Abstract

The concentration of atmospheric CO<sub>2</sub> is increasing due to emissions from burning of fossil fuels and changes in land use. Part of this “anthropogenic CO<sub>2</sub>” 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 CO<sub>2</sub> • Seawater acidity • Saturation state • Climate change • Physical carbon pump • Global warming • Biological carbon pumps • Phytoplankton • Primary production • Calcification

---

D.A. Wolf-Gladrow (✉) • B. Rost  
Alfred Wegener Institute, Helmholtz Centre for Polar and Marine Research, Bremerhaven,  
Germany  
e-mail: [dieter.wolf-gladrow@awi.de](mailto:dieter.wolf-gladrow@awi.de); [bjorn.rost@awi.de](mailto:bjorn.rost@awi.de)

## Atmospheric CO<sub>2</sub>

Atmospheric CO<sub>2</sub>, measured as partial pressure (pCO<sub>2</sub>) 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, pCO<sub>2</sub> is rising and approached values more the 40 % higher than preindustrial. CO<sub>2</sub> emissions are still increasing (currently >9 Pg C yr<sup>-1</sup>; Peters et al. 2012), and thus one has to expect pCO<sub>2</sub> 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 CO<sub>2</sub> Exchange and Ocean Carbonate Chemistry

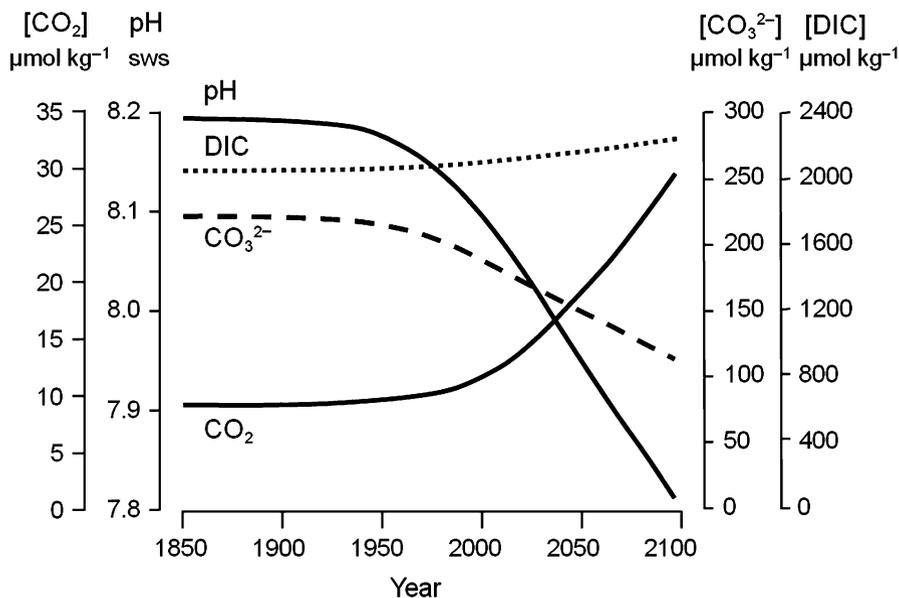
The surface ocean exchanges gases with the atmosphere. Net CO<sub>2</sub> fluxes between air and water are driven by differences in pCO<sub>2</sub> of the atmosphere and the equilibrium pCO<sub>2</sub> of seawater at a given chemical composition and temperature; at equilibrium, these two partial pressures equal each other. Starting from an equilibrium state, an increase of atmospheric CO<sub>2</sub> would lead to invasion of CO<sub>2</sub> into the ocean. In contrast to other gases like oxygen or nitrogen, CO<sub>2</sub> not just dissolves in seawater: it reacts with water to form true carbonic acid (H<sub>2</sub>CO<sub>3</sub>) that largely dissociates to bicarbonate (HCO<sub>3</sub><sup>-</sup>) and hydrogen ions (H<sup>+</sup>). CO<sub>2</sub> can also react with carbonate ions (CO<sub>3</sub><sup>2-</sup>) to form HCO<sub>3</sub><sup>-</sup> and H<sup>+</sup>. In both cases, the production of H<sup>+</sup> results in an increase of the H<sup>+</sup> concentration ([H<sup>+</sup>]) and thus to a decrease of pH, which is the negative logarithm of the H<sup>+</sup> concentration (i.e., pH = -log<sub>10</sub> [H<sup>+</sup>]).

The change in [H<sup>+</sup>] 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<sup>+</sup> per CO<sub>2</sub> molecule added”. This buffering is due to high values of total alkalinity in seawater (TA = [HCO<sub>3</sub><sup>-</sup>] + 2 [CO<sub>3</sub><sup>2-</sup>] + [B(OH)<sub>4</sub><sup>-</sup>] ± minor components). Low-TA freshwater can take up much less CO<sub>2</sub> 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 CO<sub>2</sub> emissions, causing surface ocean concentrations of CO<sub>2</sub> and HCO<sub>3</sub><sup>-</sup> to increase while CO<sub>3</sub><sup>2-</sup> 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 [CO<sub>3</sub><sup>2-</sup>]. The term “carbonation,” on the other hand, relates to overall increase in dissolved inorganic carbon (DIC), in particular [CO<sub>2</sub>].

Assuming an atmospheric pCO<sub>2</sub> of 750 μatm for the end of this century (IS92a scenario, Nakicenovic et al. 2000), surface ocean [CO<sub>2</sub>] will have almost tripled relative to preindustrial concentrations. Concomitantly, [CO<sub>3</sub><sup>2-</sup>] and pH will have



**Fig. 13.1** Predicted changes in the surface seawater carbonate chemistry in response to changes in atmospheric  $p\text{CO}_2$  assuming the IS92a scenario (Modified after Wolf-Gladrow et al. (1999))

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  $p\text{CO}_2$ . 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  $p\text{CO}_2$ -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  $p\text{CO}_2$ .

## 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  $\text{CO}_2$  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  $\text{CO}_2$  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  $\text{pCO}_2$  (e.g., Tortell et al. 2008). Such “ $\text{CO}_2$  fertilization” effects have been attributed to increased diffusive  $\text{CO}_2$  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  $\text{CO}_2$ -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  $[\text{CO}_3^{2-}]$ , which sets the saturation state ( $\Omega$ ) 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 CO<sub>2</sub> 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 CO<sub>2</sub> gradient due to respiration; hence their acid–base regulation is used to deal with high CO<sub>2</sub> 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.

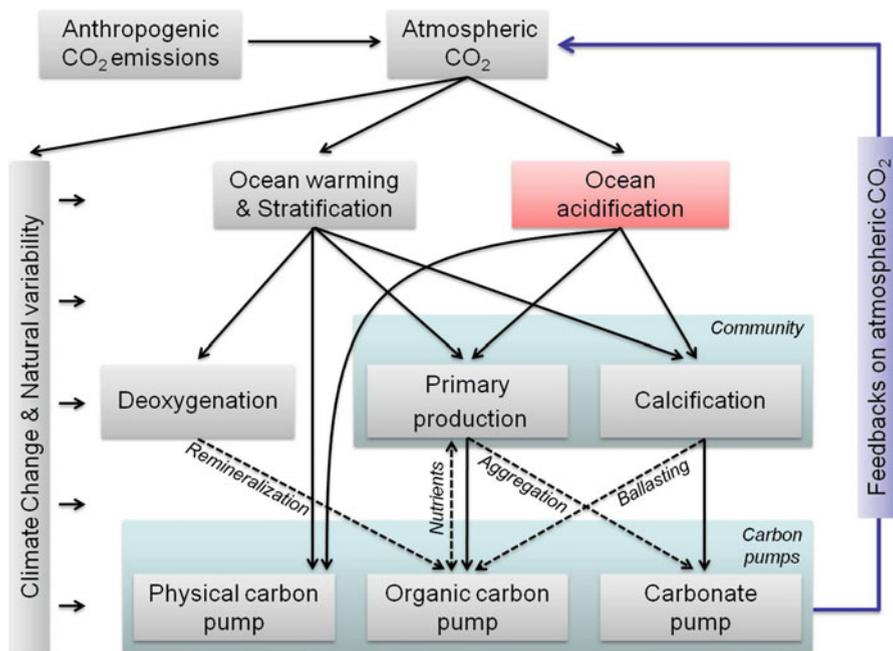
As illustrated, ocean acidification was shown to impact organisms from different trophic levels with potentially large consequences for the marine ecosystem as well as carbon cycling. For more details of biological impacts compare, for example, Gattuso and Hansson (2011).

---

## 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 pCO<sub>2</sub> would have been about twice as high (Maier-Reimer et al. 1996). Given the importance of the biological pumps for atmospheric pCO<sub>2</sub>, 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



**Fig. 13.2** Uptake of anthropogenic CO<sub>2</sub> by the ocean leads to the strengthening of the physical carbon pump. Ocean acidification is a major stressor, besides ocean warming and deoxygenation, for marine organisms and ecosystems and thus also impacts on the biological carbon pumps. *Arrows* denote direction of impact, yet the full complexity of players and processes can only be indicated

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 CO<sub>2</sub> 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 CO<sub>2</sub>. 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

- Feely RA, Sabine CL, Hernandez-Ayon JM, Janson D, Hales B (2008) Evidence for upwelling of corrosive “acidified” water onto the continental shelf. *Science* 320:1490–1492
- Gattuso J-P, Hansson L (eds) (2011) *Ocean acidification*. Oxford University Press, Oxford, 326 pp
- Gruber N (2011) Warming up, turning sour, losing breath: ocean biogeochemistry under global change. *Phil Trans R Soc A* 369:1980–1996
- Hall-Spencer JM, Rodolfo-Metalpa R, Martin S, Ransome E, Fine M, Turner SM, Rowley SJ, Tedesco D, Buia MC (2008) Volcanic carbon dioxide vents show ecosystem effects of ocean acidification. *Nature* 454:96–99
- Hönisch B, Ridgwell A, Schmidt DN, Thomas E, Gibbs SJ, Sluijs A, Zeebe R, Kump L, Martindale RC, Greene SE, Kiessling W, Ries J, Zachos JC, Royer DL, Barker S, Marchitto TM, Moyer R, Pelejero C, Ziveri P, Foster GL, Williams B (2012) The geological record of ocean acidification. *Science* 335:1058–1063
- Kranz SA, Levitan O, Richter K-U, Prášil O, Berman-Frank I, Rost B (2010) Combined effects of CO<sub>2</sub> and light on the N<sub>2</sub> fixing cyanobacterium *Trichodesmium* IMS101: physiological responses. *Plant Physiol* 154:334–345
- Kroeker KJ, Kordas RL, Crim RN, Singh GG (2010) Meta-analysis reveals negative yet variable effects of ocean acidification on marine organisms. *Ecol Lett* 13(11):1419–1434
- Le Quéré C, Rödenbeck C, Buitenhuis ET, Conway TJ, Langenfelds R, Gomez A, Labuschagne C, Ramonet M, Nakazawa T, Metz N, Gillett N, Heimann M (2007) Saturation of the Southern ocean CO<sub>2</sub> sink due to recent climate change. *Science* 316:1735–1738
- Maier-Reimer E, Mikolajewicz U, Winguth A (1996) Future ocean uptake of CO<sub>2</sub>: interaction between ocean circulation and biology. *Climate Dynam* 12:711–721
- Nakicenovic N, Alcamo J, Davis G, de Vries B, Fenhann J, Gaffin S, Gregory K, Grübler A, Jung TY, Kram T, La Rovere EL, Michaelis L, Mori S, Morita T, Pepper W, Pitcher H, Price L, Raihi K, Roehrl A, Rogner H-H, Sankovski A, Schlesinger M, Shukla P, Smith S, Swart R, van Rooijen S, Victor N, Dadi Z (2000) Emissions scenarios. A special report of Working Group III of the Intergovernmental Panel on Climate Change. Cambridge University Press, Cambridge, UK/New York, 599 pp
- Orr JC, Fabry VJ, Aumont O, Bopp L, Doney SC et al (2005) Anthropogenic ocean acidification over the twenty-first century and its impact on calcifying organisms. *Nature* 437:681–686
- Peters GP, Marland G, Le Quéré C, Boden T, Canadell JG, Raupach MR (2012) Rapid growth in CO<sub>2</sub> emissions after the 2008–2009 global financial crisis. *Nat Clim Change* 2:2–4
- Pörtner HO, Farrell AP (2008) Physiology and climate change. *Science* 322:690–692
- Tortell PD, Payne CD, Li Y, Trimborn S, Rost B, Smith WO, Risselsman C, Dunbar R, Sedwick P, di Tullio GR (2008) The CO<sub>2</sub> sensitivity of Southern Ocean phytoplankton. *Geophys Res Lett* 35, L04605
- Wisshak M, Schönberg CHL, Form A, Freiwald A (2012) Ocean acidification accelerates reef bioerosion. *PLoS ONE* 7(9):e45124

- 
- Wolf-Gladrow DA, Riebesell U, Burkhardt S, Bijma J (1999) Direct effects of CO<sub>2</sub> concentration on growth and isotopic composition of marine plankton. *Tellus B* 51(2):461–476
- Yamamoto-Kawai M, McLaughlin FA, Carmack EC, Nishino S, Shimada K (2009) Aragonite undersaturation in the Arctic Ocean: effects of ocean acidification and sea ice melt. *Science* 326:1098–1100
- Zeebe RE, Wolf-Gladrow DA (2001) CO<sub>2</sub> in seawater: equilibrium, kinetics, isotopes. Elsevier, Amsterdam, 346 pp