Atmospheric Carbon Dioxide and Changing Ocean Chemistry

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Contents

Abbreviations

CA   Carbonate alkalinity
DIC   Dissolved inorganic carbon
IPCC   Intergovernmental Panel on Climate Change
Ω_{arag} Saturation state for aragonite
Ω_{calc} Saturation state for calcite
POC   Particulate organic carbon
ppm   Parts per million
Pg   Peta gram
TA   Total alkalinity
TOC   Total organic carbon

11.1 Introduction

"*They call it pollution, we call it life*" is an infamous quote which ignores many facts about why carbon dioxide (CO_2) poses a significant problem for the ocean. But before we get to this, let's start at the beginning.

All organisms on Earth require a particular set of elements for growth. In the case of plants, these elements are needed to synthesise organic matter in a process called primary production via photosynthesis, and in the case of animals, these elements are directly assimilated by either consuming plant material or by preying on other animals. In this respect, one of the key elements is carbon. Being the molecular backbone for a number of vital organic compounds such as sugars, proteins and nucleic acids (containing genetic information), carbon can be considered as the building block of life. Similar requirements also apply to bacteria, fungi and viruses, which stand outside the plant and animal kingdoms. However, carbon is not only exchanged between organisms. There are in fact much larger reservoirs on Earth and fluxes in between, especially in the marine environment (◘ Figure 11.1). In their entirety, they are referred to as the global carbon cycle.

11.2 The Global Carbon Cycle

The largest carbon reservoir on Earth are **sedimentary rocks** in its crust and upper mantle (i.e. the lithosphere). It is approximately three orders of magnitude ($\times 1000$) larger than all other reservoirs combined (Falkowski et al. 2000), however, it has the slowest exchange rates (◘ Figure 11.1). As a consequence, it requires relatively large changes to these fluxes and typically long geologic time scales (on the order of thousands to millions of years) to significantly affect the other reservoir sizes.

The second-largest carbon reservoir are the oceans, where about 900 Pg are found in the surface ocean (1 Pg equals 10^{15} g or 10^9, or 1 billion tonnes) and approximately 37,100 Pg in the intermediate and deep ocean, mostly in the form of dissolved inorganic carbon (DIC)

(► Box 11.1). Given the relatively large exchange rates between the surface and the deep ocean and also with the atmosphere, small changes can lead to a significant redistribution, for instance in the atmosphere, which is one of the smaller reservoirs. As an example, shutting down the organic carbon pump (see below) could easily double atmospheric CO_2 levels, based on a back-on-the-envelope calculation, assuming a mean deep ocean DIC enrichment of $50 \, \mu mol \, kg^{-1}$ (compare ◘ Figure 11.2a) at an overall volume of $\sim 1.3 \times 10^{18}$ m^3 of seawater and an average depth of 3.7 km (Eakins and Sharman 2010).

On land, it is the dead organic matter stored in soils which constitutes the largest carbon reservoir. On time scales on the order of years to millennia, an important connection between these three reservoirs of easily interchangeable carbon (the soils on land, the atmosphere, and the oceans) are the living organisms. In this respect plants play a key role by taking up CO_2 via photosynthesis and utilising light as an energy source to build up biomass, a process termed **primary production**. Interestingly, net primary production which is the balance between the overall amount of carbon fixed by plants during the day and respired again to CO_2 by these organisms throughout day and night (to produce metabolic energy-sustaining cellular functioning, especially in the dark) is similar on land and at sea (~50 Pg C per year).

However, in the marine environment, this amount of carbon is being fixed by plants containing about 100 times less carbon (~3 Pg C) than those on land (450–650 Pg C). This is because on land much of the carbon stored in plants is structural (e.g. tree trunks) and only a small fraction is actively participating in carbon fixation via photosynthesis (e.g. leaves). Structural carbon is required to fight gravity and gain a competitive advantage over other plants by getting as much exposure to light as possible (imagine, for instance, a tree overshadowing the grass underneath). **In the ocean, microscopic unicellular algae (termed phytoplankton) dominate primary production**. As these organisms, float in the sunlit surface ocean and are constantly being moved by winds and currents, no structural carbon is required (or would help) in maximising light exposure.
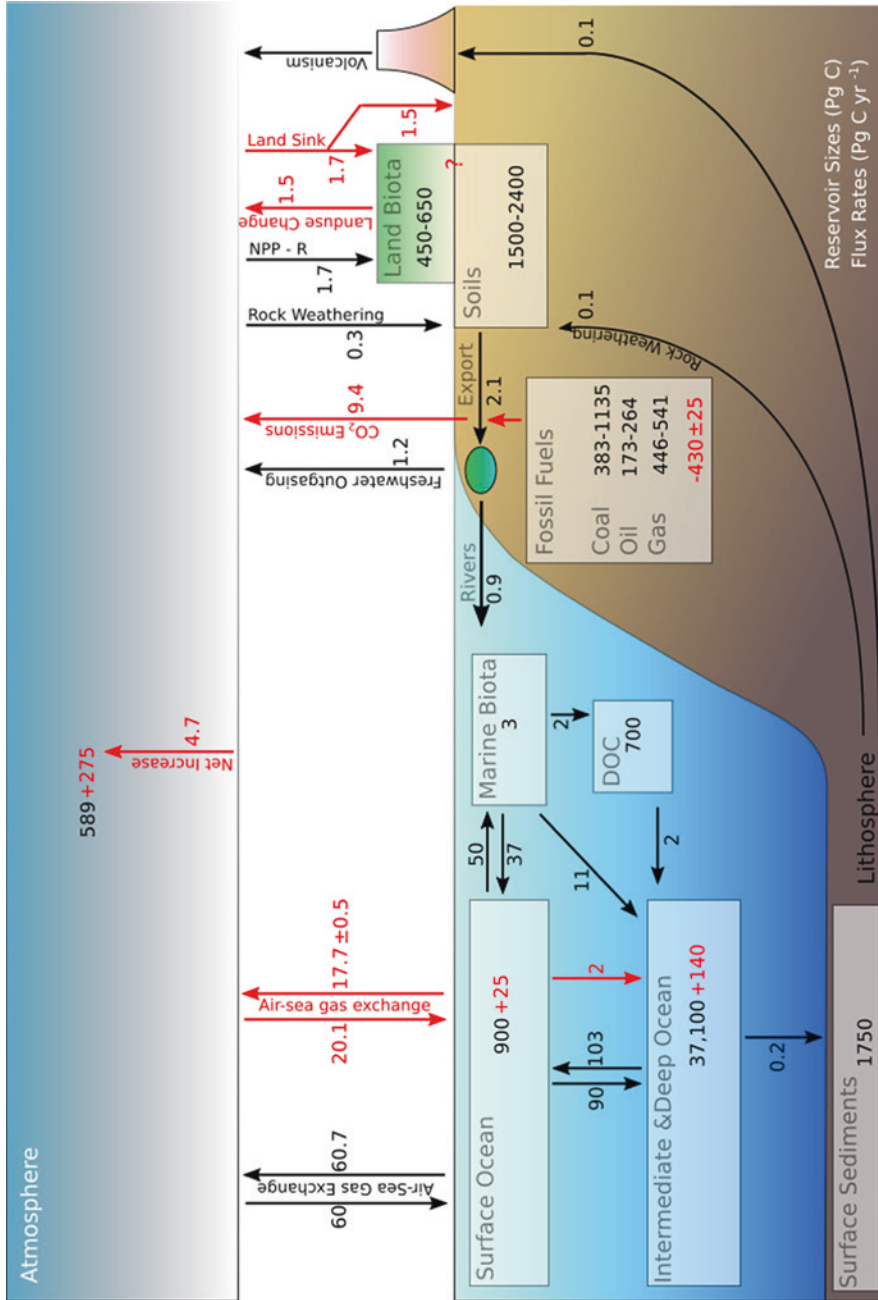
■ **Figure 11.1** Schematic diagram of the major reservoirs (Pg C) and fluxes (arrows–Pg C yr⁻¹) for a pre-industrial (reference year 1750) carbon cycle in black (IPCC 2013). In red are anthropogenic perturbations of this quasi-steady state, where changes in reservoir sizes and fluxes (period of 2008–2017) are taken from IPCC (2013) and Le Quéré et al. (2018). In this respect, the land sink has been divided into a biological and non-biological (see text for details) component (Kirschbaum et al. 2019), and the question mark highlights the unknowns concerning the overall amount of anthropogenic carbon taken up by the terrestrial biosphere. Uncertainties are only given for the anthropogenic air-sea gas exchange component and the amount of fossil fuels that have been extracted, but are representative for uncertainties in the overall budget. NPP-R refers to the balance of net primary production by plants and respiration by all other organisms. *Image:* K. Schulz

Box 11.1: Basic Carbonate Chemistry

In water carbon dioxide (CO_2) is being found as a dissolved gas ($CO_{2(aq)}$) and after hydration to H_2CO_3 and dissociation, as bicarbonate (HCO_3^-) and carbonate ions (CO_3^{2-}). As $CO_{2(aq)}$ and H_2CO_3 are chemically not separable, they are typically simply referred to as CO_2. The sum of the concentrations of all species is then dissolved inorganic carbon (DIC), defined as shown in Eq. 11.1

$$DIC = [CO_2] + [HCO_3^-] + [CO_3^{2-}] \tag{11.1}$$

The underlying acid–base equilibria are given by Eq. 11.2

$$CO_2 + H_2O \rightleftharpoons HCO_3^- + H^+ \rightleftharpoons CO_3^{2-} + 2H^+ \tag{11.2}$$
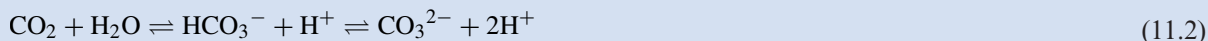
Another key concept in carbonate chemistry is that of total alkalinity (TA), which can be defined as the excess of proton acceptors over proton donors (Dickson 1981). Essentially, TA can be seen as the buffering capacity of the ocean to resist changes in pH. TA can be expressed as (Zeebe and Wolf-Gladrow 2001) Eq. 11.3:

$$\begin{aligned} TA = {}& [HCO_3^-] + 2[CO_3^{2-}] + [B(OH_4)^-] + [OH^-] \\ & + [HPO_4^{2-}] + 2[PO_4^{3-}] + [H_3SiO_4^-] \\ & + [NH_3] + [HS^-] - [H^+]_F - [HSO_4^-] \\ & - [HF^-] - [H_3PO_4] + \cdots - \cdots \end{aligned} \tag{11.3}$$

with the last two terms accounting for minor components of alkalinity such as conjugate bases of organic acids, and minor proton donors.

In this interlinked system, the relative contribution of the three DIC components to the overall concentration is controlled by pH (◘ Figure 11.2). However, it worth noting that any change to the concentration of one of the DIC components, or TA, will equally lead to changes in pH.
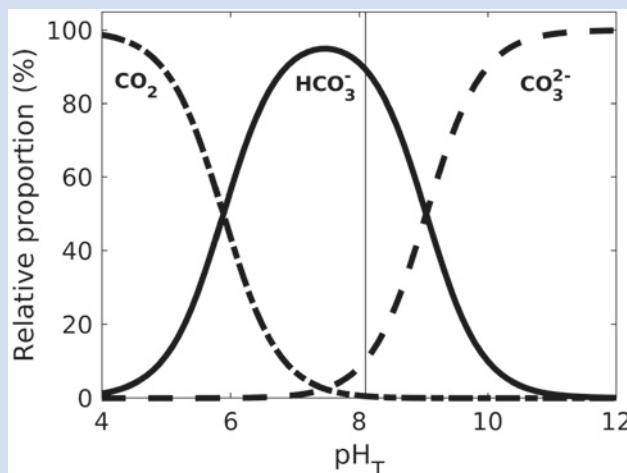
◘ **Figure 11.2**   ▶ Box 11.1 Relative contributions of CO_2, HCO_3^- and CO_3^{2-} to overall DIC as a function of pH (total hydrogen ion scale), also known as Bjerrum plot and calculated using stoichiometric equilibrium constants for carbonic acid from Mehrbach et al. (1973) and refitted by Dickson and Millero (1987)

Before the beginning of the Industrial Revolution, this global cycling of carbon was thought to have been in quasi-steady state (Pongratz et al. 2009), meaning that the flow of carbon in and out of a reservoir was roughly balanced (◘ Figure 11.1). However, significant changes have occurred since then, but before we come to these we shall have a closer look at carbon cycling within the ocean.

11.3 The Physical and Biological Carbon Pumps

The so-called **carbon pumps** describe the flux of dissolved inorganic carbon and total alkalinity from the ocean surface to depth. They are operating against a concentration gradient, and their relative strengths drive the direction of CO_2 air-sea gas exchange (◘ Figure 11.3b).

The physical carbon pump is based on increasing CO_2 solubility when warmer waters cool. Subsequently when sea ice forms at cold high latitudes in the North Atlantic and around Antarctica, the DIC-rich surface waters become particularly dense (due to high salinity) and sink (◘ Figure 11.3b). Such deep-water formation at high latitudes is responsible for large-scale ocean circulation with water masses flowing at depth from the North to the South Atlantic, and into the Indian and Pacific Oceans where they are eventually subject to upwelling and return as surface currents back to the North Atlantic. The **biological carbon pump** can be split into two; the organic carbon (or soft tissue) pump, and the carbonate counter pump. As the name suggests the latter operates in the opposite way to the former in terms of atmospheric CO_2 uptake of the surface ocean (◘ Figure 11.3b).

The **organic carbon pump** is driven by marine phytoplankton (microscopic unicellular plants) which, as mentioned above, fix CO_2 into organic matter in the sun-lit surface ocean via photosynthesis. Most of the carbon will end up in the particulate rather than the dissolved organic fraction and rain down to the ocean floor when particles have a higher density than the surrounding seawater. During downward transport most of the particulate organic carbon (POC) will be converted back to CO_2 by bacterial respiration and only a fraction of the ~11 Pg exported each year will be buried in sediments (compare ◘ Figures 11.1 and 11.3b).

The **carbonate counter pump** is driven by calcium carbonate ($CaCO_3$) formation of open ocean organisms, mainly calcifying phytoplankton (coccolithophores), and zooplankton (foraminifera and pteropods). As the precipitation of $CaCO_3$ shifts the carbonate chemistry equilibrium towards lower pH and
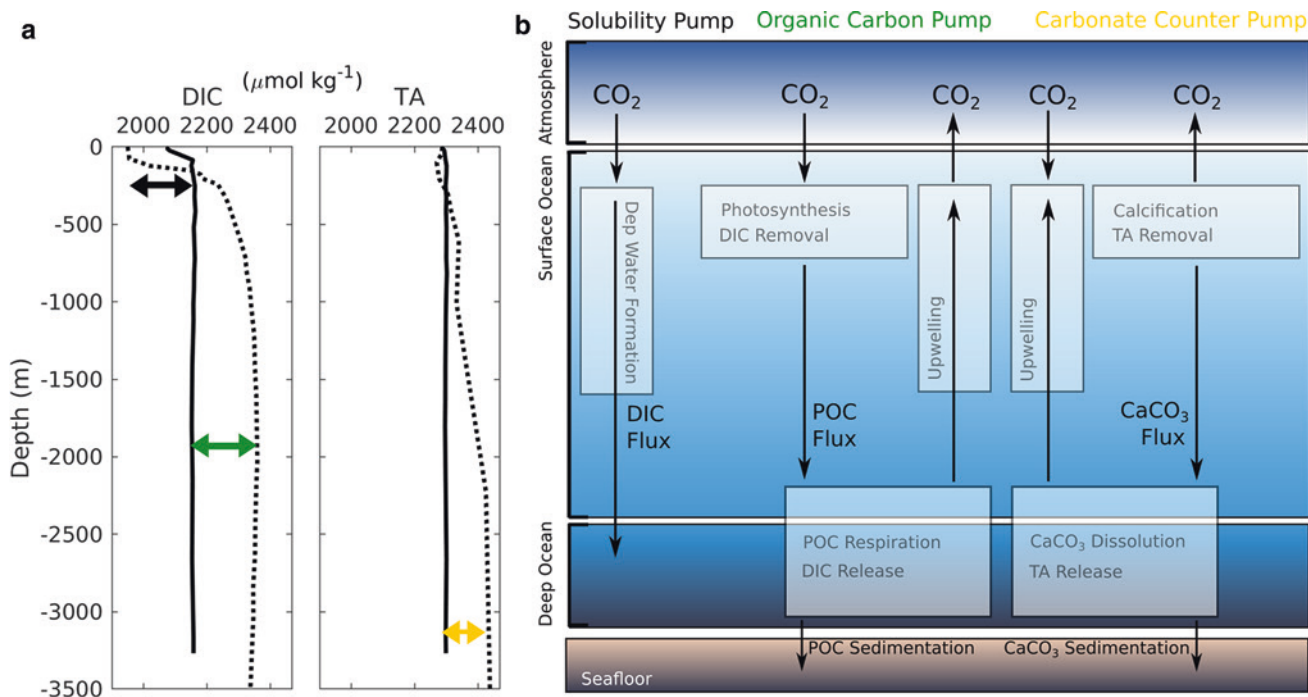

◘ **Figure 11.3** **a** Depth profiles of dissolved inorganic carbon (DIC) and total alkalinity (TA) in the North Atlantic at 57.3° N/39.5° W (solid line) and the Tropical Pacific at 15° N/135° W (dotted line) taken from Alvarez (1997) and Goyet et al. (1997), respectively, and **b** a schematic of the two carbon pumps. They can be divided into the physical solubility pump (black arrow in **a**), and the organic carbon (green arrow in **a**) and carbonate counter pumps (yellow arrow in **a**). The reason for higher DIC and TA at depth in the Pacific compared to the Atlantic profiles is the amount of time without contact with the atmosphere and the water age. In general, the older the water mass the more particulate organic carbon (POC) respiration and calcium carbonate ($CaCO_3$) dissolution will have taken place at depth. *Image*: K. Schulz

hence higher CO_2 (▶ Box 11.2), the ocean's storage capacity for the latter is reduced. At present, $CaCO_3$ is a stable mineral in most of the surface ocean, an important fact as some organisms critically rely on these minerals (see ▶ Section 11.4.2 for details). Being denser than seawater, however, there is a steady rain of $CaCO_3$ to the sea floor, estimated at approximately 1 Pg C per year. About 90% of this will dissolve as the saturation state decreases with pressure at depth and waters eventually become undersaturated. Although $CaCO_3$ formation in the surface ocean has an immediate opposite effect on CO_2 air-sea gas exchange in comparison to photosynthesis, $CaCO_3$ is thought to strengthen the efficiency of the organic carbon pump as aggregates of POC and the much denser $CaCO_3$ will sink more rapidly (Klaas and Archer 2002; De La Rocha and Passow 2014). This would move respiration to deeper layers and keep the CO_2 produced away from atmospheric contact for longer time. As a consequence, this would increase the surface to depth DIC gradient and allow for more atmospheric CO_2 to be stored at depth.

Whether the positive effects of ballasting on oceanic CO_2 uptake outweigh the negative effects of $CaCO_3$ production is difficult to reconcile, however, models suggest that they may cancel each other out (e.g. Barker et al. 2003; Kvale et al. 2021). While the two carbon pumps govern biogeochemical element cycling in the ocean, they are part of a bigger picture, the **global carbon cycle**, which is currently perturbed by human activities.

11.4 Human-Induced Changes to the Global Carbon Cycle

Since the beginning of the Industrial Revolution in the late eighteenth century, the burning of fossil fuels such as oil, gas and coal, as well as cement production, has come with emissions of the greenhouse gas carbon dioxide (CO_2). Together with changes in land-use and deforestation, these anthropogenic emissions have significantly changed the flow of carbon between land, ocean and atmosphere, impacting respective reservoir sizes (▢ Figure 11.1). From the ~430 Pg of carbon stemming from fossil fuels and cement production, ~275 Pg have been accumulating in the atmosphere. With ~235 Pg estimated to originate from land-use changes and ~165 Pg having entered the oceans, the terrestrial carbon sink is estimated to be ~225 Pg. For a long time, this has been considered the result of CO_2 – enhanced photosynthesis coupled with vast amounts of nitrogen and phosphorus being released into the environment as fertiliser, enhancing growth in the last 100 years. Although this simple mass balance

is similar to estimates from various dynamic vegetation models (Le Quéré et al. 2018), it has been proposed recently that almost half of the current annual land sink for anthropogenic carbon is not linked to an increase in terrestrial biomass storage. Rather, it comprises fossil fuels which are not turned into CO_2 (i.e. plastics and bitumen), harvested wood products and CO_2 being absorbed by cement carbonation in concrete structures. Hence, at the moment, it is difficult to put a number on the biological component of the terrestrial carbon sink.

Nevertheless, the human-induced changes to the global carbon cycle in general, and the atmosphere in particular are driving climate change by affecting Earth's radiative balance, causing mean surface temperatures to increase. While this is an accepted fact within the scientific community after decades of research–the first assessment report on climate change by the Intergovernmental Panel on Climate Change (IPCC) dates back to the 1990s and the most recent report was released in 2021 (IPCC 1990, 2021)–there are groups of activists campaigning against this scientific consensus. A memorable anecdote is the release of a television advertisement by the Competitive Enterprise Institute, a neoconservative think tank in May 2006. This video appeared to be targeting Al Gore's film *An Inconvenient Truth*, which was about to be released in cinemas worldwide at the time and highlighted the connections between a fossil fuel-based economy and climate change. In an attempt to dismiss the negative effects of increasing atmospheric CO_2 levels on Earth's climate system and referring to the fact that plants utilise CO_2 in photosynthesis for growth, the advertisement culminated in the claim "*CO_2: They call it pollution, we call it life!*".

Today we are in a situation where it appears highly unlikely to be able to stabilise global temperatures at 1.5 °C above pre-industrial levels until the end of this century (IPCC 2018). This was a goal adopted by 179 states that ratified the United Nations Paris Agreement in 2015, in order to keep the threats of temperature-driven global climate change (e.g. ice melt, sea level rise, and intensification of extreme weather events) within manageable boundaries. However, these are not the only issues with increasing levels of atmospheric CO_2, as it also has a direct impact on the world's oceans.

11.4.1 Ocean Acidification

In the last 250 years, atmospheric CO_2 levels have steadily increased from 280 ppm (parts per million) to 417 ppm in 2022 (Friedlingstein et al. 2022). As a result of equilibration at the air-sea interface, substan-
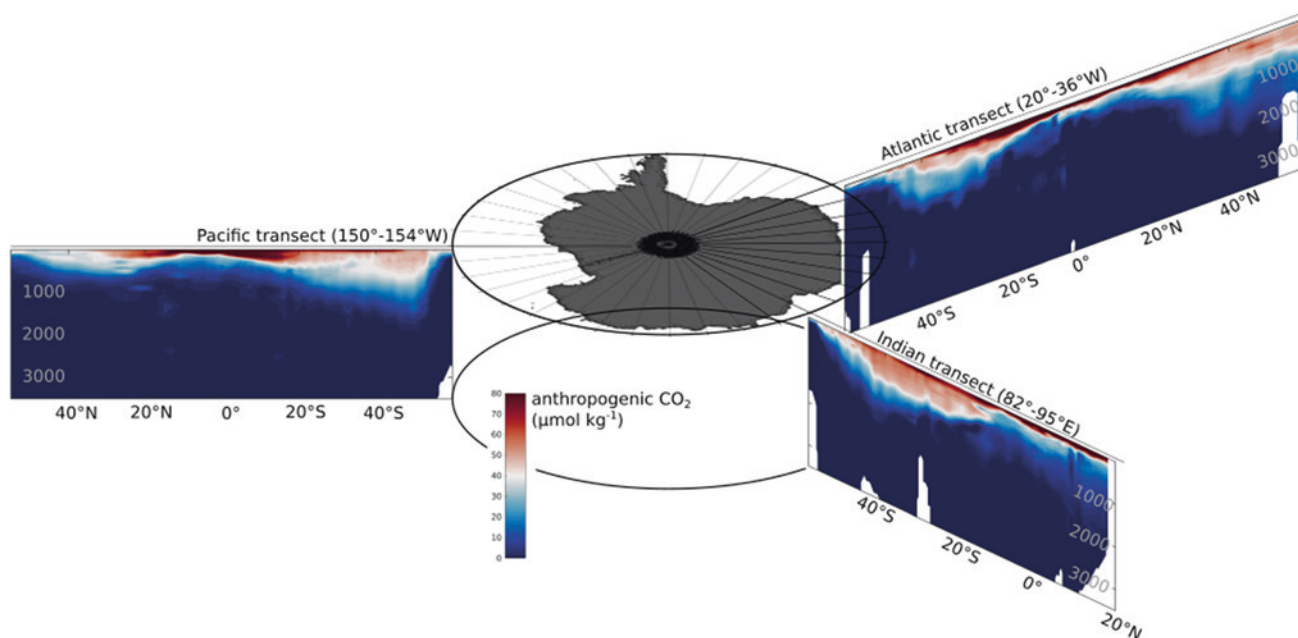
■ **Figure 11.4** Concentrations of anthropogenic CO_2 found in all three major ocean basins, centred around the Antarctic continent (depth in metres). Calculations from measured oxygen, DIC, salinity and temperature follow the principles outlined in Sarmiento and Gruber (2006) and are described in detail in Schulz and Riebesell (2011). Data for the Pacific (Feely et al. 2013a; b), Atlantic (Wanninkhof et al. 2013; Peltola et al. 2013) and Indian ocean (Feely et al. 2013c; d) are from transects of the CLIVAR repeat hydrography program. *Image*: K. Schulz

tial amounts of this anthropogenic CO_2 have also made its way into the ocean (■ Figure 11.4). When CO_2 dissolves in seawater it forms carbonic acid, which reduces its pH (Equation 11.2). This is known as **ocean acidification and has been coined the evil twin of climate change** (Pelejero et al. 2010). The pH of the ocean has already dropped by ~0.1 units since the Industrial Revolution, which is equivalent to a ~30% increase in acidity (note that the pH scale is logarithmic). This drop in pH has changed carbonate chemistry speciation (▶ Box 11.1), with potentially significant implications for a number of key species in the ocean.

11.4.2 Potential Effects of Ocean Acidification on Key Organisms and Processes of the Marine Carbon Cycle

With the realisation that ongoing ocean acidification might pose a threat to marine organisms and ecosystems, research into the potential biological responses has grown exponentially during the last two decades. Today the number of studies is probably in the thousands (compare Gattuso and Hansson 2011). Since it is beyond the scope of this Chapter to cover all of them, we will focus on key groups and processes in terms of impact on global carbon cycling.

One of the first groups suspected to be affected by ocean acidification was calcium **carbonate ($CaCO_3$) producing (or calcifying) organisms.** The reasoning was that the CO_2 – induced reduction in pH would reduce carbonate ion concentrations (▶ Box 11.2) and hence substrate availability for calcification, in turn negatively affecting $CaCO_3$ precipitation rates (Broecker and Takahashi 1966). Today, a majority of studies (including meta-analyses) have indeed found that calcification rates in most marine taxa are negatively impacted by ocean acidification. This includes hard corals, calcifying phytoplankton (a very important taxon for marine carbon cycling at the base of marine food webs and for marine carbon cycling ■ Figure 11.5), algae, foraminifera, pteropods and molluscs (Gattuso and Hansson 2011; Kroeker et al. 2010, 2013; Schulz et al. 2017), although it has to be acknowledged that there are species-specific differences and sensitivities.

In this respect, it is interesting to note that there is still an ongoing debate on the physiological mechanisms underlying the susceptibility of calcification to ocean acidification. **Calcification** is a process under tight cellular control and involves diffusion and transport of ions across membranes. While there is a consensus that calcification rates are a function of the internal saturation state at the site of $CaCO_3$ precipitation, the key question is by which external bulk seawater carbonate chemistry parameter(s) it is gov-
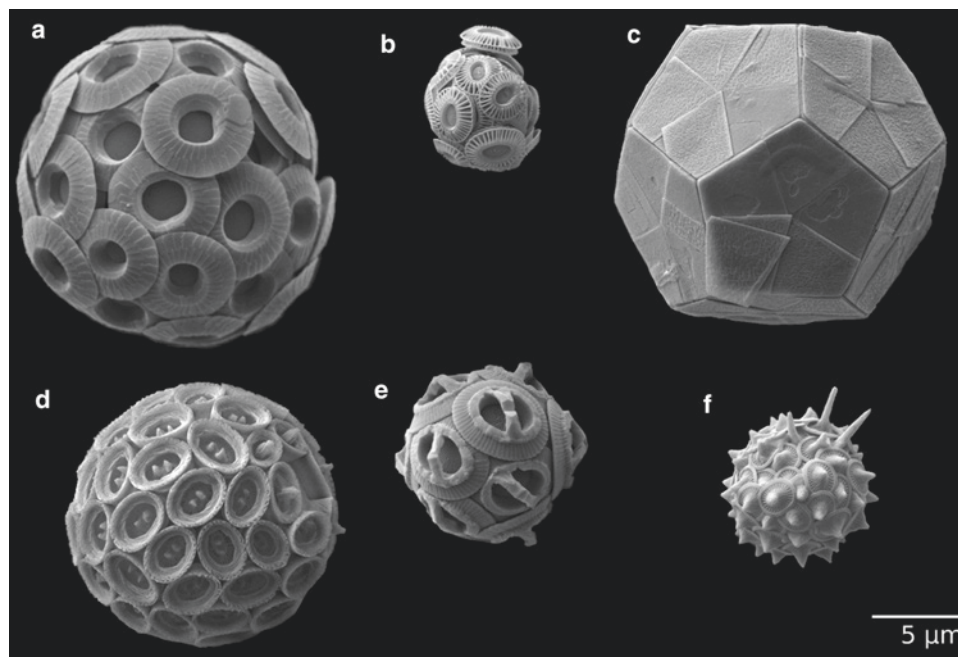
■ Figure 11.5   Calcifying phytoplankton divsersity in the modern ocean, exemplified by **a** *Umbilicosphaera sibogae*, **b** *Emiliania huxleyi*, **c** *Braarudosphaera bigelowii*, **d** *Coronosphaera binodata*, **e** *Gephyrocapsa oceanica* and **f** *Acanthoica quattrospina*. *Images*: M. Dawes. For details on coccolithophore-global carbon cycle interactions see Rost and Riebesell (2004)

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erned. For coccolithophores, there is experimental evidence that it is decreasing seawater pH levels which are unfavourable for calcification (e.g. Bach et al. 2015). The underlying principle is a reduction in the internal to external electrochemical proton gradient, which is thought to increase the costs of removing the protons (e.g. Gafar et al. 2019 and references therein) that are generated by $CaCO_3$ precipitation (▶ Box 11.2). These basic principles could also be the mechanisms underlying the sensitivity of calcification in other marine organisms. While this idea has recently been advocated (Cyronak et al. 2016a, b), it has also been contested (Waldbusser et al. 2016).

The other key group of marine organisms (when it comes to global carbon cycling) are **photoautotrophs**. Since they harness the energy of light to fix CO_2 in photosynthesis, it might be expected that this process could profit from ocean acidification. Indeed, there is (with the exception of calcifying algae) a trend towards increased photosynthesis in response to ocean acidification. However, it appears that photosynthesising calcifiers (such as corals and coccolithophores) might benefit less than non-calcifying groups such as the main contributor to ocean primary productivity [i.e. diatoms, fleshy algae and seagrasses (Kroeker et al. 2010, 2013)]. Again, it is important to stress that sensitivities are species-specific.

While most of the experiments on the effects of **ocean acidification** on marine calcification and primary production have been conducted on single species, to predict future changes it is necessary to include important factors on the **ecosystem level** such as species interaction (e.g. predation, and competition for resources). This requires either larger-scale manipulative in-situ studies or manipulative incubations with entire communities. A good example of the former are experiments which showed that net calcification rates of an entire reef–including a variety of calcifiers ranging from corals to coralline algae and foraminifera in sediments–were decreasing with decreasing pH and vice versa (Albright et al. 2016, 2018). The future survival of coral reef ecosystems depends on this intricate budget, **taking into account all $CaCO_3$ precipitation and dissolution processes**. In addition, mass balance calculations including corals and sediments suggest that below a seawater aragonite saturation state of 2.55, reefs with 5% coral cover might become net dissolving (Eyre et al. 2018). Depending on the future CO_2 emission scenario, this threshold could be reached well before the turn of this century (IPCC 2013), in particular for reefs that experience upwelling of naturally CO_2-rich deep waters, such as documented along the East Australian coast, amplifying ocean acidification (Schulz et al. 2019).

Box 11.2: Calcium Carbonate

The formation of the mineral calcium carbonate ($CaCO_3$) leads to redistributions in carbonate chemistry speciation, decreasing pH and CO_3^{2-} ions, and increasing CO_2 concentrations. This can be understood by realising that CO_3^{2-} ion concentrations can be expressed as TA-DIC, upon simplifying Eq. 11.1 and 11.3 as shown in Eq. 11.4:

$$TA \approx CA = [HCO_3^-] + 2[CO_3^{2-}] \tag{11.4}$$

with CA denoting carbonate alkalinity and as shown in Eq. 11.5:

$$DIC \approx [HCO_3^-] + 2[CO_3^{2-}] \tag{11.5}$$

These are valid approximations in typical seawater as CA contributes about 95% to total alkalinity and CO_2 less than 1% to DIC. Since the formation of $CaCO_3$ reduces TA twice as much as DIC, the difference between them, i.e. the CO_3^{2-} ion concentration, decreases. This is equivalent to shifting carbonate chemistry speciation towards the left in a Bjerrum plot (◘ Figure 11.1), leading to decreasing pH and increasing CO_2 concentrations. It is acknowledged that the actual acid-base re-equilibration is more complex as overall DIC concentrations are changing (assumed constant in a Bjerrum plot), but the change of direction is the same (for details see Zeebe and Wolf-Gladrow 2001).

Ocean Acidification and Saturation State

Carbonate ion availability is also reduced by ocean acidification (Equation 11.2). This is crucial in governing the saturation state of the mineral calcium carbonate ($CaCO_3$) which has two main polymorphs, i.e. the more soluble aragonite and the less soluble calcite. Whether these minerals are stable in seawater is given by their respective saturation states, defined as shown in Eq. 11.6:

$$\Omega_{arag/calc} = \frac{[Ca^{2+}][CO_3^{2-}]}{K_{sp}} \tag{11.6}$$

with K_{sp} denoting the temperature and salinity dependent solubility product in equilibrium for aragonite or calcite, and $[Ca^{2+}]$ and $[CO_3^{2-}]$ denoting respective concentrations in seawater. Hence, seawater Ω levels above One are indicative of stable mineral conditions in the water column, while at levels below One $CaCO_3$ would start to dissolve.

When it comes to assessing the effects of ocean acidification on the main drivers of marine primary productivity, mesocosms have proven an invaluable tool. They are incubation units large enough to house a community of organisms on multiple trophic levels (e.g. primary producers, primary consumers, and secondary consumers). Most **mesocosm studies** to date have not found positive effects of ocean acidification on autotrophic biomass build-up (see Bach et al. 2017; Maugendre et al. 2017; Schulz et al. 2017, and references therein). This suggests that either the products of potentially enhanced photosynthesis (compare single-species experiments) are effectively transferred up the trophic ladder by grazing or are remineralised by bacterial respiration, or that a change in species composition is having a buffering effect. Although at this stage the underlying mechanisms are not fully understood, changes in species composition have been found in most experiments. A re-occurring pattern in this respect is that when effects are found, small picoeukaryote abundances are positively affected and coc-colithophore abundances are negatively affected by ocean acidification (Schulz et al. 2017). In regard to diatoms, their abundances are mostly positively affected, with shifts towards larger species (Bach and Taucher 2019). These findings have the potential to significantly change marine carbon cycling with feedbacks to the climate system (see below). However, **changes in phytoplankton community composition** can also change the transfer efficiency to higher trophic levels and affect fish production, either through changes in food quality (Rossoll et al. 2012) or by disrupting the vital link between primary producers and fish (i.e. the zooplankton community through toxin-producing harmful algal blooms.

Last but not least, it is not only necessary to scale up experiments in space and time to include the required realism with species interaction, competition and natural variability, but also to assess the interactive effects of other environmental drivers which are changing in concert with ongoing ocean acidification (Riebesell and Gattuso 2014)–often referred to as anthropo-

genic stressors. These include, but are not limited to, increasing surface ocean temperatures which enhance stratification and hence reduce mixed layer depths, which is thought to increase light but decrease nutrient availability for primary production.

11.4.3 Potential Effects of Ocean Acidification on Biogeochemical Element Cycling

Changes to the efficiency and/or strength of the biological carbon pumps are bound to affect air-sea CO_2 gas exchange (compare ◘ Figure 11.3). Hence, ongoing ocean acidification-driven changes would constitute a feedback loop, either amplifying or dampening increasing atmospheric CO_2 levels (Riebesell et al. 2009). As described above, the mineral ballasting ($CaCO_3$ or biogenic silica) of particulate organic matter produced in the sun-lit surface ocean, which is otherwise nearly neutrally buoyant, enhances the transport of organically bound CO_2 into the deep ocean. Hence, reductions in $CaCO_3$ production there are thought to negatively impact this export flux (e.g. Armstrong et al. 2002; Boyd and Doney 2002). Experimental assessment, however, has proven difficult, in part due to the large distances involved (1000s of metres). However, on smaller scales (10s of metres) in mesocosm experiments, ocean acidification has been found to significantly reduce the bloom-forming potential of the cosmopolitan coccolithophore *Emiliania huxleyi* (◘ Figure 11.5) which in turn reduced the amount of sedimenting organic carbon by approximately a quarter (Riebesell et al. 2018). As this was directly related to reductions in sinking speed velocities with reduced $CaCO_3$ production (Bach et al. 2016), it might be reasonable to assume this mechanism is also operating in the real ocean. When it comes to biogenic silica production by diatoms, the other important ballast mineral, it is more complicated as of a more variable response to ocean acidification (Bach and Taucher 2019). Although, overall contributions of diatoms to primary production have recently been projected to decrease in the future ocean (Trèguer et al. 2018), with the exception of the Southern Ocean, in which however, the amount of cellular silica ballast produced by diatoms have been found to decrease with ocean acidification (Petrou et al. 2019).

The shift from larger to smaller sized picophytoplankton as a result of ocean acidification found in a number of experiments (see Schulz et al. 2017 and references therein), could have a similar effect on the flux of organic carbon to depth and hence atmospheric CO_2 levels. This is based on observations of lower export efficiencies at a number of open ocean sites with significant picophytoplankton community contributions, although considerable variability exists locally and seasonally (see De La Rocha and Passow 2014 for a review).

In summary, experiments on the effects of ocean acidification on surface ocean carbon cycling imply that positive could outweigh negative feedbacks, amplifying increasing levels of atmospheric carbon dioxide.

11.5 Outlook

Without a reduction in anthropogenic CO_2 emissions, the future ocean will continue to become more acidic. Depending on CO_2 emission scenario extrapolations to the year 2100 suggest a further decrease in pH of ~0.2–0.3 units (IPCC 2013). The direction and magnitude of all the feedback mechanisms associated with ocean acidification are currently difficult to project, but clearly there will be significant effects on certain organisms and ecosystems.

To successfully reduce anthropogenic CO_2 emissions will require a combination of legislative and technological advances. Several significant steps have been made in trying to curb the emissions of CO_2, such as the UN Paris Agreement and national arrangements such as Canada's Greenhouse Gas Pollution Price Act. However, despite these important steps, CO_2 emissions as of today are still increasing (Le Quéré et al. 2018), highlighting the need to further strengthen our efforts. In terms of technological advances, the efficiency of the leading multi-junction cell solar panels has reached ~46% (Green et al. 2018), and renewable energy output is increasing globally (as demand has unfortunately too), supplying almost 30% of global electricity demand in 2020 (IEA 2020). With continued advancement in technology, along with the implementation of legislative tools, a zero-emission future is achievable, but if it will be quick enough remains to be seen.

11.6 Summary

Carbon is considered the building block of life. It is exchanged between organisms, but there are much larger reservoirs and fluxes on Earth, especially in the marine environment. Carbon reservoirs include sedimentary rocks in the Earth's crust and upper mantle (primarily), the oceans, the soils on land, and to a lesser extent the atmosphere. Significant changes have occurred since the Industrial Revolution, when global cycling of carbon (the flow of carbon in and out of a reservoir) was near balanced in a quasi-steady state (Pongratz et al. 2009).

Carbon pumps are either biological or physical and operate against a concentration gradient. Their relative strengths drive the direction of CO_2 air-sea gas exchange, and govern biogeochemical element cycling in the ocean. The physical carbon pump is driven by increasing CO_2 solubility when warmer waters cool. When sea ice forms in the North Atlantic and around Antarctica, the DIC-rich surface waters increase in density and sink. This is driving large-scale ocean circulation.

The **biological carbon pump** includes the **organic carbon pump** and the **carbonate counter pump**, and these operate in an opposite direction in terms of atmospheric CO_2 uptake. The organic carbon pump is driven by the constant rain of particulate organic matter from the surface ocean, where it had been produced by photosynthesis. During sinking, most particulate organic carbon will be converted back to CO_2 by bacterial respiration. The carbonate counter pump is driven by $CaCO_3$ formation by marine organisms, whereby precipitation of $CaCO_3$ shifts the carbonate chemistry equilibrium towards lower pH and hence a higher CO_2 concentration.

Anthropogenic CO_2 emissions since the Industrial Revolution, along with changes in land-use and deforestation, have significantly altered the flow of carbon between land, oceans, and the atmosphere. These human-induced changes to the global carbon cycle in general, and the atmosphere in particular, are driving current climate and ocean change. In the last 250 years, atmospheric CO_2 levels have increased from 280 to 417 ppm (in 2022). Substantial amounts of CO_2 have made their way into the ocean causing ocean acidification, with a reduction in the pH of surface waters by ~0.1 units (equivalent to a 30% increase in acidity) as of today. This will **most likely have increasing implications for numerous marine keystone species**. Furthermore, experiments on the effects of ocean acidification on surface ocean carbon cycling suggest that positive feedback effects are likely to amplify increasing levels of atmospheric CO_2. A combination of legislative and technological advances is needed to reduce anthropogenic CO_2 emissions and mitigate global climate/ocean change.

11.7 Study Questions and Activities

1. Describe how pH influences the proportions of CO_2, CO_3^{2-} and HCO_3^- in water and vice versa.
2. Discuss the various carbon pumps and how they influence marine carbon cycling.
3. Describe how $CaCO_3$ formation in the surface ocean has the opposite effect to photosynthesis on CO_2 air-sea gas exchange.
4. Explain the meaning of "saturation state", and how this is relevant to calcifying marine organisms.
5. Summarise The United Nations Paris Agreement, and report up-to-date information regarding its implementation.

References

Albright R, Caldeira L, Hosfelt J, Kwiatkowski L, Maclaren JK, Mason BM, Nebuchina Y, Ninokawa A, Pongratz J, Ricke KL, Rivlin T (2016) Reversal of ocean acidification enhances net coral reef calcification. Nature 531:362–365
Albright R, Takeshita Y, Koweek DA, Ninokawa A, Wolfe K, Rivlin T, Nebucchina Y, Young J, Caldeira K (2018) Carbon dioxide addition to coral reef waters suppresses net community calcification. Nature 555:516–519
Alvarez MS (1997) Carbon dioxide, hydrographic, and chemical data obtained during the R/V discovery cruise in the North Atlantic Ocean during WOCE Section A25 (7 August–17 September 1997). US Department of Energy, Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, Oak Ridge, Tennessee. ► https://doi.org/10.3334/CDIAC/otg.WOCE_A25. ► http://cdiac.ornl.gov/ftp/oceans/CARINA/Discovery/74DI230/
Armstrong RA, Lee C, Hedges JI, Honjo S, Wakeham SG (2002) A new mechanistic model for organic carbon fluxes in the ocean based on the quantitative association of POC with ballast minerals. Deep-Sea Res II 49:219–236
Bach LT, Taucher J (2019) CO_2 effects on diatoms: a synthesis of more than a decade of ocean acidification experiments with natural communities. Ocean Sci 15:1159–1175
Bach LT, Riebesell U, Gutowska MA, Federwisch L, Schulz KG (2015) A unifying concept of coccolithophore sensitivity to changing carbonate chemistry embedded in an ecological framework. Prog Oceanogr 135:125–138
Bach LT, Boxhammer T, Larsen A, Hildebrandt N, Schulz KG, Riebesell U (2016) Influence of plankton community structure on the sinking velocity of marine aggregates. Glob Biogeochem Cycles 30:1145–1165
Bach LT, Alvarez-Fernandez S, Hornick T, Stuhr A, Riebesell U (2017) Simulated ocean acidification reveals winners and losers in coastal phytoplankton. PLoS ONE 12(11):e0188198
Barker S, Higgins JA, Elderfield H (2003) The future of the carbon cycle: review, calcification response, ballast and feedback on atmospheric CO_2. Philos Trans Roy Soc Lond a: Math Phys Eng Sci 361(1810):1977–1999
Boyd PW, Doney SC (2002) Modelling regional responses by marine pelagic ecosystems to global climate change. Geophys Res Lett 29(16):53-2–53-4
Broecker WS, Takahashi T (1966) Calcium carbonate precipitation on the Bahama Banks. J Geophys Res 171:1575–1602
Cyronak T, Schulz KG, Jokiel PL (2016a) The Omega myth: what really drives lower calcification rates in an acidifying ocean. ICES J Mar Sci 73:558–562
Cyronak T, Schulz KG, Jokiel PL (2016b) Response to Waldbusser et al. (2016b): 'Calcium carbonate saturation state: on myths and this or that stories'. ICES J Marine Sci 7:569–571
Dickson AG (1981) An exact definition of total alkalinity and a procedure for the estimation of alkalinity and total inorganic carbon from titration data. Deep-Sea Res 28:609–623
Dickson AG, Millero FJ (1987) A comparison of the equilibrium constants for the dissociation of carbonic acid in seawater media. Deep-Sea Res 34:1733–1743

De La Rocha C, Passow U (2014) 8.4—The biological pump. In: Holland H, Turekian K (eds) Treatise on geochemistry, vol 8, 2nd edn. Elsevier, Amsterdam, pp 93–122

Eakins BW, Sharman GF (2010) Volumes of the world's oceans from ETOPO1. NOAA National Geophysical Data Center, Boulder, CO. Available at ► https://www.ngdc.noaa.gov/mgg/global/etopo1_ocean_volumes.html. Accessed 22 Feb 2022

Eyre BD, Cyronak T, Drupp P, De Carlo EH, Sachs JP, Andersson AJ (2018) Coral reefs will transition to net dissolving before end of century. Science 359:908–911

Falkowski P, Scholes RJ, Boyle E, Canadell J, Canfield D, Elser J, Gruber N, Hibbard K, Hoegberg P, Linder S, Mackenzie FT, Moore B III, Pedersen T, Rosenthal Y, Seitzinger S, Smetacek V, Steffen W (2000) The global carbon cycle: a test of our knowledge of Earth as a system. Science 290:291–296

Feely RA, Sabine CL, Millero FJ, Langdon C, Fine RA, Bullister JL, Hansell DA, Carlson CA, McNichol A, Key RM, Byrne RH, Wanninkhof R (2013a) Dissolved inorganic carbon (DIC), total alkalinity, dissolved organic carbon (DOC), chlorofluorocarbons, temperature, salinity and other hydrographic and chemical variables collected from discrete samples and profile observations during the R/V Roger Revelle Cruise CLIVAR_P16S_2005 (EXPOCODE 33RR20050109) in the South Pacific Ocean from 2005-01-09 to 2005-02-19 (NODC Accession 0108095). Version 3.3. National Oceanographic Data Center, NOAA. Dataset. ► https://doi.org/10.25921/09v7-bq08

Feely RA, Sabine CL, Millero FJ, Langdon C, Fine RA, Bullister JL Hansell DA, Carlson CA, McNichol A, Key RM, Byrne RH, Wanninkhof R (2013b) dissolved inorganic carbon (DIC), total alkalinity, pH on total scale, partial pressure of carbon dioxide (pCO$_2$), temperature, salinity and other hydrographic and chemical variables collected from discrete samples and profile observations during the R/V Thomas G. Thompson Cruise CLIVAR_P16N_2006 (EXPOCODE 325020060213) in the Pacific Ocean from 2006-02-13 to 2006-03-30 (NODC Accession 0108062). Version 2.2. National Oceanographic Data Center, NOAA. Dataset. ► https://doi.org/10.25921/bvaz-zm17

Feely RA, Sabine CL, Dickson AG, Wanninkhof R, Hansell DA (2013c) Dissolved inorganic carbon (DIC), total alkalinity, temperature, salinity and other variables collected from discrete sample and profile observations during the R/V Roger Revelle Cruise CLIVAR_I08S_2007 (EXPOCODE 33RR20070204) in the Indian Ocean from 2007-02-04 to 2007-03-17 (NODC Accession 0108119). Version 2.2. National Oceanographic Data Center, NOAA. Dataset. ► https://doi.org/10.3334/CDIAC/OTG.CLIVAR-I08S-2007

Feely RA, Sabine CL, Millero FJ, Wanninkhof R, Hansell DA (2013d) Dissolved inorganic carbon (DIC), total alkalinity, pH on sea water scale, temperature, salinity and other variables collected from discrete sample and profile observations during the R/V Roger Revelle Cruise CD139, CLIVAR I09N_2007 (EXPOCODE 33RR20070322) in the Indian Ocean from 2007-03-22 to 2007-05-01 (NODC Accession 0110791). Version 2.2. National Oceanographic Data Center, NOAA. Dataset. ► https://doi.org/10.3334/CDIAC/OTG.CLIVAR-I09N-2007

Friedlingstein P et al. (2022) Global Carbon Budget 2022. Earth Syst Sci Data 14:3811–4900. ► https://essd.copernicus.org/articles/14/4811/2022/essd-14-4811-2022-discussion.html

Gafar NA, Eyre BD, Schulz KG (2019) Particulate inorganic to organic carbon production as a predictor for coccolithophorid sensitivity to ongoing ocean acidification. Limnol Oceanogr Lett 4:62–70

Gattuso J-P, Hansson L (2011. Ocean acidification. Oxford University Press, Oxford, p 408

Goyet C, Key RM, Sullivan KF, Tsuchiya M (1997) Carbon dioxide, hydrographic, and chemical data obtained during the R/V Thomas Washington Cruise TUNES-1 in the equatorial Pacific Ocean (WOCE Section P17C). ORNL/CDIAC-99, NDP-062. Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, Oak Ridge, Tennessee. ► https://doi.org/10.3334/CDIAC/otg.ndp062

Green MA, Hishikawa Y, Dunlop ED, Levi DH, Hohl-Ebinger J, Ho-Baillie AWY (2018) Solar cell efficiency tables (version 51). Prog Photovolt Res Appl 26(1):3–12

IEA (International Energy Agency) (2020) Global energy review 2020. ► https://www.iea.org/reports/global-energy-review-2020/renewables. Accessed 11 Jan 2022

IPCC (Intergovernmental Panel on Climate Change) (1990) Climate Change. In: Houghton J, Jenkins G, Ephraums J (eds) The IPCC Scientific Assessment, Working Group I. Cambridge University Press, Cambridge, p 351. Available at ► https://www.ipcc.ch/site/assets/uploads/2018/03/ipcc_far_wg_I_full_report.pdf. Accessed 7 Feb 2022

IPCC (Intergovernmental Panel on Climate Change) (2013) In: Stocker TF, Qin D, Plattner G-K, Tignor M, Allen SK, Boschung J, Nauels A, Xia Y, Bex V, Midgley PM (eds) Climate Change 2013: the physical science basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change. Cambridge University Press, Cambridge, p 1535. Available at ► https://www.ipcc.ch/report/ar5/wg1/. Accessed 7 Feb 2022

IPCC (Intergovernmental Panel on Climate Change) (2018) Summary for policymakers. In: Masson-Delmotte V, Zhai P, Pörtner HO, Roberts D, Skea J, Shukla PR, Pirani A, Moufouma-Okia W, Péan C, Pidcock R, Connors S, Matthews JBR, Chen Y, Zhou X, Gomis XI, Lonnoy E, Maycock T, Tignor M, Waterfield T (eds) Global warming of 1.5 °C. An IPCC special report on the impacts of global warming of 1.5 °C above pre-industrial levels and related global greenhouse gas emission pathways, in the context of strengthening the global response to the threat of climate change, sustainable development, and efforts to eradicate poverty. World Meteorological Organization, Geneva, p 24. Available at ► https://www.ipcc.ch/sr15/chapter/spm/. Accessed 7 Feb 2022

IPCC (Intergovernmental Panel on Climate Change) (2021) In: Masson-Delmotte V, Zhai P, Pirani A, Connors SL, Péan C, Berger S, Caud N, Chen Y, Goldfarb L, Gomis MI, Huang M, Leitzell K, Lonnoy E, Matthews JBR, Maycock TK, Waterfield T, Yelekçi O, Yu R, Zhou B (eds) Climate Change 2021: the physical science basis. Contribution of Working Group I to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change. Cambridge University Press, Cambridge (in press)

Kirschbaum MUF, Zeng G, Ximenes F, Giltrap DL, Zeldis JR (2019) Towards a more complete quantification of the global carbon cycle. Biogeosciences 16:831–846

Klaas C, Archer DE (2002) Association of sinking organic matter with various types of mineral ballast in the deep sea: implications for the rain ratio. Glob Biogeoch Cycles 16(4):63-1–63-14

Kroeker KJ, Kordas RL, Crim RN, Singh GG (2010) Meta-analysis reveals negative yet variable effects of ocean acidification on marine organisms. Ecol Lett 13:1419–1434

Kroeker KJ, Kordas RL, Crim R, Hendriks IE, Ramajo L, Sing GS, Duarte CM, Gattuso J (2013) Impacts of ocean acidification on marine organisms: quantifying sensitivities and interaction with warming. Glob Change Biol 19:1884–1896

Kvale K, Koeve W, Mengis N (2021) Calcifying phytoplankton demonstrate an enhanced role in greenhouse atmospheric CO$_2$ regulation. Front Mar Sci 7:583989

Le Quéré C, Andrew RM, Friedlingstein P, Sitch S, Hauck J, Pongratz J, Pickers PA, Korsbakken JI, Peters GP, Canadell JG, Arneth A, Zheng B (2018) Global carbon budget 2018. Earth Syst Sci Data 10(4):2141–2194

Maugendre L, Guieu C, Gattuso J-P, Gazeau F (2017) Ocean acidification in the Mediterranean Sea: Pelagic mesocosm experiments. a synthesis. Estuarine Coastal Shelf Sci 186:1–10

Mehrbach C, Culberson CH, Hawley JE, Pytkowicz RM (1973) Measurement of the apparent dissociation constants of carbonic acid in seawater at atmospheric pressure. Limnol Oceanogr 18:897–907

Pelejero C, Calvo E, Hoegh-Guldberg O (2010) Paleo-perspectives on ocean acidification. Trends Ecol Evol 25(6):332–344

Peltola E, Wanninkhof R, Feely RA, Hansell DA, Castle RD, Greeley D, Zhang J-Z, Millero FJ, Gruber N, Bullister JL, Taylor G (2013) Partial pressure (or fugacity) of carbon dioxide, dissolved inorganic carbon, pH, alkalinity, temperature, salinity and other variables collected from discrete sample and profile observations using alkalinity titrator, CTD and other instruments from NOAA Ship RONALD H. BROWN in the North Atlantic Ocean and South Atlantic Ocean from 2003-06-04 to 2003-08-11 (NODC Accession 0108061). Version 3.3. National Oceanographic Data Center, NOAA. Dataset. ► https://doi.org/10.3334/CDIAC/OTG.NDP085

Petrou K, Baker KG, Nielsen DA, Hancock AM, Schulz KG, Davidson AT (2019) Acidification diminishes diatom silica production in the Southern Ocean. Nat Clim Chang 9:781–786

Pongratz J, Reick CH, Raddatz T, Claussen M (2009) Effects of anthropogenic land cover change on the carbon cycle of the last millennium. Glob Biogeochem Cycles 23:Gb4001

Riebesell U, Gattuso JP (2014) Lessons learned from ocean acidification research. Nat Clim Change 5:12–14

Riebesell U, Körtzinger A, Oschlies A (2009) Sensitivities of marine carbon fluxes to ocean change. Proc Natl Acad Sci 106(49):20602–20609

Riebesell U, Aberle-Malzahn N, Achterberg EP, AlguerólMuñiz M, Alvarez-Fernandez S, Arístegui J, Bach LT, Boersma M, Boxhammer T, Guan W, Haunost M (2018) Toxic algal bloom induced by ocean acidification disrupts the pelagic food web. Nat Clim Change 8:1082–1086

Rossoll D, Bermúdez R, Hauss H, Schulz KG, Riebesell U, Sommer U Winder M (2012) Ocean acidification-induced food quality deterioration constrains trophic transfer. PloS one 0034737

Rost B, Riebesell U (2004) Coccolithophores and the biological pump responses to environmental changes. In: Thierstein H, Young J (eds) Coccolithophores: from molecular processes to global impact. Springer, Berlin, pp 99–125

Sarmiento JL, Gruber N (2006) Ocean biogeochemical dynamics. Princeton University Press, Princeton, p 503

Schulz KG, Riebesell U (2011) Versauerung des Meerwassers durch anthropogenes CO_2. In: Lozán J, Graßl H, Reise K (eds) Warnsignal Klima: Die Meere - Änderungen und Risiken. Universität Hamburg, Hamburg, pp 160–163

Schulz KG, Bach LT, Bellerby RGJ, Bermúdez R, Büdenbender J, Boxhammer T, Czerny J, Engel A, Ludwig A, Meyerhöfer M, Larsen A, Paul AJ, Sswat M, Riebesell U (2017) Phytoplankton blooms at increasing levels of atmospheric carbon dioxide: experimental evidence for negative effects on prymnesiophytes and positive on small picoeukaryotes. Front Marine Sci 4:64

Schulz KG, Hartley S, Eyre BD (2019) Upwelling amplifies ocean acidification on the East Australian Shelf: implications for marine ecosystems. Front Mar Sci 6:636

Trèguer P, Bowler C, Moriceau B, Dutkiewicz S, Gehlen M, Aumont O, Bittner L, Dugdale R, Finkel Z, Iudicone D, Jahn O, Guidi L, Lasbleiz M, Leblanc K, Levy M, Pondaven P (2018) Influence of diatom diversity on the ocean biological carbon pump. Nat Geosci 11:27–37

Waldbusser G, Hales B, Haley BA (2016) Calcium carbonate saturation state: on myths and this or that stories. ICES J Mar Sci 73:569–571

Wanninkhof R, Doney SC, Castle RD, Millero FJ, Bullister JL, Hansell DA, Warner MJ, Langdon C, Johnson GC, Mordy C (2013) Partial pressure (or fugacity) of carbon dioxide, dissolved inorganic carbon, pH, alkalinity, temperature, salinity and other variables collected from discrete sample and profile observations using alkalinity titrator, barometric pressure sensor and other instruments from NOAA Ship RONALD H. BROWN in the South Atlantic Ocean, South Pacific Ocean and Southern Oceans from 2005-01-11 to 2005-02-24 (NODC Accession 0108153). Version 3.3. National Oceanographic Data Center, NOAA. Dataset. ► https://doi.org/10.3334/CDIAC/OTG.NDP087

Zeebe RE, Wolf-Gladrow D (2001) CO_2 in seawater: equilibrium, kinetics, isotopes. Elsevier oceanography series, vol 65. Elsevier Science BV, Amsterdam, p 346