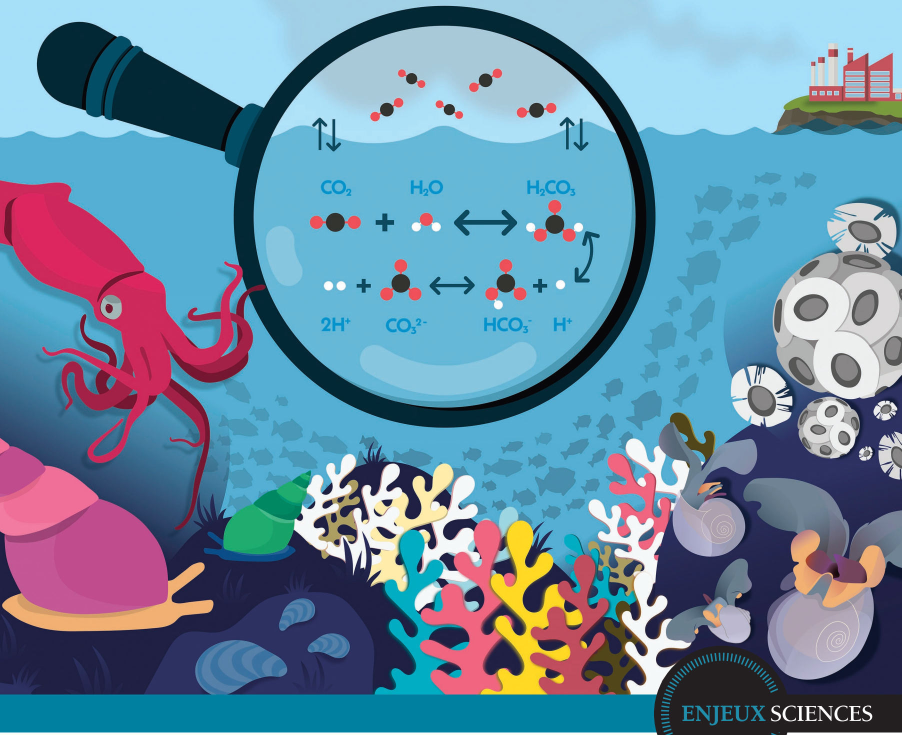

ENJEUX SCIENCES

OCEAN ACIDIFICATION

UNDERSTANDING THE EFFECTS, EXPLORING THE SOLUTIONS

FABRICE PERNET AND FRÉDÉRIC GAZEAU

éditions Quæ

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Introduction
Why a book on ocean acidification?

Human-induced climate change is now a proven fact, no longer in doubt in the scientific community. Heat waves, droughts and floods, storms and hurricanes of unprecedented power are current manifestations of this ongoing climate change, where exceptional events are becoming more and more frequent. The increasing combustion of fossil fuels such as coal, gas and oil, as well as deforestation for agriculture and urbanisation, are enlarging the concentration of greenhouse gases in the atmosphere, warming the planet. Of the greenhouse gases produced by this combustion, carbon dioxide (CO_2) is by far the most abundant.

Climate change is not the only consequence of rising atmospheric CO_2 concentrations. Anthropogenic CO_2 is also partly absorbed by the oceans, where it is transformed into carbonic acid, causing "ocean acidification". This phenomenon really emerged in the scientific literature in the early 2000s, becoming one of the most studied topics in marine science over the last twenty years. Through its effects on water chemistry, ocean acidification has multiple consequences for the marine world and its inhabitants, and consequently for the biological resources on which we depend to live.

However, ocean acidification, often referred to as "the other CO_2 problem" in reference to global warming, remains largely unknown to the general public. The few times the media mention this phenomenon, it is to ask whether we will still be eating oysters in 2100! While this question is relevant, as it suggests that these animals are sensitive to acidification, it deserves to be considerably broadened. In other words, the idea is to understand not only the world *we live from*, but also the world *we live in*, so that we can face the new climate regime with lucidity and pragmatism[1].

The aim of this book is to take a comprehensive look at ocean acidification by answering ten simple questions. It reviews the biogeochemical foundations of acidification; past, current and future trends; impacts on organisms, marine ecosystems and humans; and finally, remediation options and scientific perspectives.

The problem of ocean acidification is transdisciplinary, and finds its answers in biogeochemistry, marine biology and ecology, evolution, aquaculture and fisheries, as well as economics and sociology. May this book make accessible to as many people as possible the magnitude of this little-known phenomenon, which is nonetheless essential to understanding future changes.

---

[1] Bruno Latour and Nikolak Schultz, 2022. *Mémo sur la nouvelle classe écologique*, Paris, La Découverte, coll. Les Empêcheurs de penser en rond, 96 p.

WHAT IS OCEAN ACIDIFICATION?

Human influence on the environment dates back to the origin of hominids, almost 3 million years ago. The hunting activities of Paleolithic hunter-gatherers led to the extinction of numerous animal species. Among the most emblematic examples are the extinctions of the megafauna of the last Ice Age, from the woolly mammoth of northern Eurasia to the giant wombats of Australia.

The advent of sedentarisation and agriculture 10,000 to 12,000 years ago reinforced human influence on the environment. During this period, humans intensified the exploitation of natural resources and transformed landscapes through deforestation and the development of irrigation. However, pre-industrial humans lacked the technological or organisational capacity to rival or dominate the great forces of nature. Their impacts remained largely local and transitory, well within the limits of natural environmental variability (Steffen *et al.*, 2007).

From the 18th century onwards, industrialisation turned humanity into a true geological and morphological force, as a number of scientists recognised early on. In 1873, for example, Stoppani described human activity as “a new telluric force whose power and universality may be compared with the greatest forces of the Earth” (quoted in Steffen *et al.*, 2007). Stoppani was already talking about the so-called “anthropozoic” era. However, it was not until the 2000s that the term “Anthropocene” appeared, referring to the current geological epoch marked by humanity’s central role in the great biogeochemical cycles of the elements (Crutzen and Stoermer, 2000).

In this chapter, we will see how the discovery and exploitation of vast quantities of carbon energy buried in the Earth’s subsoil have led to profound transformations in human societies, with major consequences for the carbon cycle, the Earth’s climate and ocean chemistry.

MACHINES, FOSSIL FUELS AND PEOPLE

Since the Industrial Revolution, whose origins broadly correspond to the invention of the internal combustion engine by James Watt in 1758, the number of humans populating the Earth and their level of wealth has increased exponentially (Steffen *et al.*, 2015). The use of more sophisticated and efficient machines greatly increased human capacity to produce goods, communicate and travel, enabling the emergence of the consumer society we know today.

The proliferation of machines and their widespread use in all sectors of production — agriculture, industry and service — was made possible by the discovery of abundant, free energy resources: fossil fuels such as coal, gas and oil. These natural energy resources, non-renewable on our timescales, were formed from plants and animals that lived hundreds of millions years ago. Fossil fuels are carbon-rich compounds that release an extraordinary amount of energy when burned, in addition to carbon dioxide, the famous "CO_2" which we are all familiar with.

This CO_2, naturally present in the atmosphere, is chemically inert, meaning it cannot degrade or react with other compounds to transform itself. Consequently, the CO_2 formed by the combustion of fossil fuels needed to sustain human activities accumulates in the atmosphere or is exchanged with the planet's other compartments, namely the land and the ocean.

GREENHOUSE EFFECT AND CO_2

The sun continuously emits energy in the form of visible light and ultraviolet rays. Some of this energy is absorbed by the Earth's surface, producing heat. The Earth then re-emits this heat as infrared radiation. Certain atmospheric gases, known as greenhouse gases, such as water vapour, CO_2, methane (CH_4), nitrous oxide (N_2O) and ozone (O_3), absorb part of the infrared radiation. The absorption of infrared radiation by these atmospheric gases has the effect of trapping heat in the atmosphere and raising the planet's temperature: this is the greenhouse effect. Without the greenhouse effect, the average global temperature would be – 18°C instead of the current 15°C.

Human activities produce large quantities of greenhouse gases, mainly in the form of CO_2, which increase the amount of heat at the Earth's surface and cause climate change. Despite the stated intentions of governments, CO_2 emissions have been rising steadily for decades, from 2 billion tonnes of CO_2 in 1900, to 6 billion in 1950 and over 37 billion in 2022, a 20-fold increase in just over a century[2]. Our greenhouse gas emissions have never fallen from one year to the next in the last twenty years, except during the financial crisis of 2008 and the COVID-19 pandemic in 2020.

Before the industrial era, the concentration of CO_2 in the atmosphere was around 280 parts per million (ppm), or 0.028% of the gases contained in the atmosphere. Since then, it has exceeded 400 ppm in 2013. The concentration of CO_2 in the atmosphere is currently monitored at numerous sites worldwide, but a series of measurements, started in the 1950s on the Mauna Loa volcano in Hawaii (USA), serves as a benchmark (Figure 1). At the time of writing (August 2023), the CO_2 concentration at this site is 419.68 ppm[3].

Analysis of the composition of ice cores extracted from the Antarctic ice sheet provides information on the climate and composition of the atmosphere going back up to about 800,000 years (Figure 1; Lüthi *et al.*, 2008). Air bubbles trapped in these ice cores at various depths (down to 3,600 m) enable us to assess the atmospheric concentration at the time of formation of these older and younger layers of ice, and thus to go back in time (Figure 1). These glacial climate archives show that CO_2 concentrations have varied periodically between around 180 and 280 ppm, corresponding to glacial and interglacial episodes respectively. These analyses also show that current atmospheric CO_2 concentrations and their rate of increase since 1950 are without historical precedent.

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[2] https://robbieandrew.github.io/GCB2022/PNG/s11_2022_FossilFuel_and_Cement_emissions_1990.png

[3] https://keelingcurve.ucsd.edu

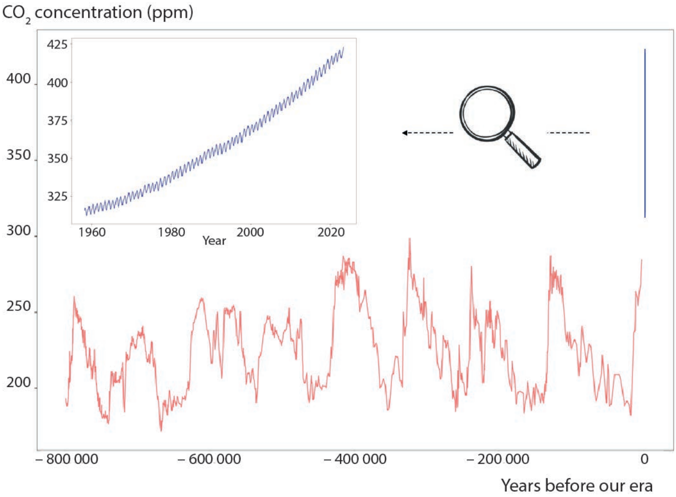

Figure 1. 800,000-year trend in atmospheric CO_2 concentration.

CO_2 concentrations are either estimated from the analysis of air bubbles trapped in ice collected in Antarctica (in red; https://www.ncei.noaa.gov/access/paleo-search/study/17975), or measured since the late 1950s at the Mauna Loa volcano in Hawaii (in blue on the right and enlarged on the graph inserted on the left; https://keelingcurve.ucsd.edu).

SOME LIKE IT HOT!

The increase in global surface temperature observed for decades now leaves no room for doubt. According to the World Meteorological Organisation, every decade since the 1980s has been warmer than the previous one. The average global temperature in 2022 was around 1.15°C higher than its pre-industrial level (period between 1850 and 1900), and the last eight years (2015-2022) are the warmest ever recorded in the world[4]. Although it is always difficult to establish links between cause and effect, the Intergovernmental Panel on Climate Change (IPCC) unambiguously reiterates in its latest synthesis report that global warming is indeed caused by greenhouse gas emissions linked to human activities (IPCC, 2023). In recent years, the

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[4] Press release dated January 12, 2023, available on the WMO website.

media have made the subject their own, resulting in a collective awareness of the phenomenon and its consequences.

THE FATE OF ANTHROPOGENIC CO_2

More than half of the CO_2 emitted into the atmosphere by human activities is captured by the terrestrial and oceanic compartments, considerably limiting the increase in the greenhouse effect and global warming. Terrestrial plants consume CO_2 to form organic matter from the energy provided by solar radiation, releasing oxygen in the process. This is the process of photosynthesis. The Global Carbon Project[5], which annually assesses anthropogenic CO_2 emissions and their redistribution, estimates that, on the one hand, the terrestrial biosphere has captured around 12.8 billion tonnes of CO_2, or 31.4% of emissions linked to human activities in 2021 (Friedlingstein *et al.*, 2022).

On the other hand, around 25% of atmospheric CO_2 dissolves in seawater and is exported to the deep ocean through biological and physical processes. At the ocean surface, dissolved CO_2 is captured by phytoplankton and transformed into organic matter, which eventually sinks to the deep layers, far from the atmosphere. Additionally, dissolved CO_2 is transported by currents from the surface to the bottom *via* the thermohaline circulation, which stirs up water on a global scale, both at the surface and in the deep ocean. The thermohaline circulation is driven by density differences in seawater, which depend on temperature and salinity, hence the term “thermos” for temperature and “halin” for salinity. At high latitudes in the Northern Hemisphere, surface water cools, increasing its density. This water, now denser and therefore heavier than the layers below, sinks to the depths, taking with it the CO_2 it has exchanged with the atmosphere at the ocean surface. The CO_2 thus exported to depths continues its journey southwards through the deep layers of the ocean, following the thermohaline circulation, and is temporarily removed from exchanges with the atmosphere. It is estimated that it takes between 1,000 and

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[5] https://www.globalcarbonproject.org/carbonbudget/

1,500 years for a water molecule to complete this entire circuit. As a result, these waters eventually rise back to the surface and exchange the CO_2 with the atmosphere. The oceanic carbon pump has stored around 10.5 billion tonnes of CO_2, or 26.2% of our emissions in 2021 (Friedlingstein *et al.*, 2022).

When CO_2 dissolves in seawater, the entire chemistry of dissolved inorganic carbon is altered. Dissolved inorganic carbon, or DIC, includes CO_2, bicarbonate ions (HCO_3^-) and carbonate ions (CO_3^{2-}). The chemical reactions that result from CO_2 dissolution are relatively complex and will only be briefly described here (for more information, see Zeebe and Wolf-Gladrow, 2001).

Some of the CO_2 absorbed by the ocean reacts with water (H_2O) to form carbonic acid (H_2CO_3), according to the reaction:

$$CO_{2(aq)} + H_2O \rightleftharpoons H_2CO_3 \text{ (eq. 1)}$$

Carbonic acid is unstable in water and rapidly dissociates into hydrogen ions (or protons H^+) and bicarbonate ions (HCO_3^-):

$$H_2CO_3 \rightleftharpoons HCO_3^- + H^+ \text{ (eq. 2)}$$

Some of the protons released by carbonic acid can react with carbonate ions (CO_3^{2-}) to form bicarbonate ions once again:

$$H^+ + CO_3^{2-} \rightleftharpoons HCO_3^- \text{ (eq. 3)}$$

As the production of hydrogen ions leads to an increase in acidity, the consequence of the absorption of anthropogenic CO_2 by the ocean has been dubbed “ocean acidification”.

pH, or hydrogen potential, is a measure of acidity on a scale of 0 to 14, calculated from proton concentration ($pH = -\log[H^+]$). The pH scale is logarithmic, meaning that a deviation of one unit indicates a division or multiplication of the proton concentration by ten. A liquid is said to be acidic or basic when the pH is respectively below or above 7, the so-called neutral pH value that characterises pure water. The surface ocean is slightly basic, with an average pH of 8.1. The projected decrease over the coming centuries will not cause the surface ocean to fall below neutrality. Strictly speaking, the ocean will not become acidic, nor will it turn into lemon juice! Ocean acidification consists of a shift in pH towards the acidic pole, without actually reaching it.

The above equations clearly show that the uptake of CO_2 by the ocean is not simply a matter of increasing its acidity. Firstly, the addition of CO_2 leads to a rise in the concentration of dissolved inorganic carbon. Secondly, there is an elevation in the proportion of bicarbonate ions and a decrease in the proportion of carbonate ions. These changes are illustrated in Figure 2, which shows the relative proportions of each molecular species of dissolved inorganic carbon as a function of pH. At the ocean surface, dissolved inorganic carbon is composed of 87.6% bicarbonate ions, 11.9% carbonate ions and 0.5% CO_2 at a temperature of 25°C, a salinity of 35 and a pH level of 8.1. As pH decreases, acidity increases; this equilibrium shifts to the left of the graph, with more bicarbonate ions, more CO_2, and fewer carbonate ions.

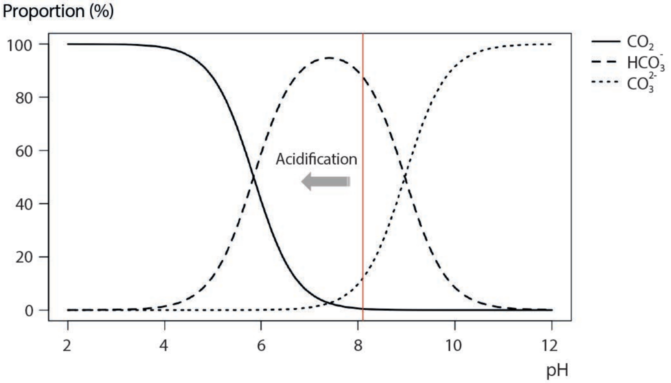

Figure 2. Bjerrum plot showing the relative contribution of carbon dioxide (CO_2), bicarbonate ions (HCO_3^-) and carbonate ions (CO_3^{2-}) to dissolved inorganic carbon (DIC) in seawater, as a function of pH.

The red vertical line represents the average pH of the current surface ocean. In this example, the temperature is set at 15°C and the salinity at 35. The graph is based on the Bjerrum function in the R package "seacarb" (Gattuso *et al.*, 2023).

All these changes in seawater chemistry have repercussions for marine organisms, which we will detail in Chapter 5. In particular, the drop in carbonate ions is problematic for calcifying organisms, such as corals and molluscs, which use this compound along with calcium ions (Ca^{2+}) to produce calcium carbonate ($CaCO_3$ or limestone), the building block of their shells or skeletons. This process, known as “calcification” or “biomineralization”, can be summed up in the following chemical equation:

$$Ca^{2+} + CO_3^{2-} \rightleftharpoons CaCO_3 \text{ (eq. 4)}$$

Given the equilibrium that exists between the different species of inorganic carbon dissolved in seawater, the balance equation for calcification and its inverse, dissolution, is written as follows:

$$Ca^{2+} + 2HCO_3^- \rightleftharpoons CaCO_3 + CO_2 + H_2O \text{ (eq. 5)}$$

Thus, calcification consumes bicarbonate ions and produces CO_2 while limestone dissolution produces bicarbonate ions and consumes CO_2. These changes therefore imply a decrease in pH when calcification is favoured and an increase when dissolution dominates.

The ability of organisms to precipitate calcium carbonate depends on the degree to which the seawater is saturated with this element, known as the “saturation state” and expressed by the Greek letter omega (Ω). When the saturation level is greater than 1, calcium carbonate tends to precipitate, i.e. forms a solid molecule. Conversely, when water saturation is less than 1, calcium carbonate tends to dissolve. The saturation state of seawater (Ω) is calculated from the following equation:

$$\Omega = \frac{[Ca^{2+}]\,[CO_3^{2-}]}{[Ca^{2+}]_{sat}\,[CO_3^{2-}]_{sat}} \text{ (eq. 6)}$$

The saturation state is therefore defined as the ratio between observed calcium and carbonate ion concentrations and those expected when the solution is at saturation (*sat*). As a result, ocean acidification leads to a drop in saturation levels, to the point of favouring the dissolution of limestone structures rather than their precipitation in certain regions.

Thus, the uptake of atmospheric CO_2 of human origin by the ocean leads to a series of chemical changes that come under the heading of “ocean acidification”, with potential consequences for marine life. Awareness of this “other CO_2 problem” has lagged behind that of global warming.

HOW LONG HAVE WE BEEN TALKING ABOUT OCEAN ACIDIFICATION?

The discovery of the ocean acidification process is closely linked to the recent understanding of the chemical principles of acidity and the development of precise tools for measuring this parameter.

JUST ACIDITY!

The first theory of acidity is attributed to French chemist Antoine Lavoisier, who at the end of the 18th century defined an acid as a compound containing oxygen. This inaccurate theory was corrected a century later by Svante August Arrhenius, who defined an acid as a substance which, when placed in aqueous solution, releases hydrogen or proton ions (H^+), whereas a base is a substance which, when placed in aqueous solution, releases hydroxide ions (OH^-). The Nobel Prize-winning Swedish chemist, who pioneered the understanding of the greenhouse effect, extended the concept of acidity to carbon dioxide (CO_2), which reacts with water molecules to form carbonic acid (H_2CO_3) (eq. 1, Chapter 1, p. 12). Arrhenius' work laid the foundations for understanding CO_2 as an acid and its impact on chemical equilibria in various aqueous systems, including seawater.

The concept of pH or "hydrogen potential" was introduced as a quantitative measure of a solution's acidity in 1909 by biochemist Søren Peter Lauritz Sørensen. The first pH measurements in seawater date back to this period. However, these early measurements cannot be used to study acidification trends, as they are too rare and not always reliable.

HOW IS pH MEASURED?

Since the beginning of the 20th century, the pH of seawater has been measured using glass electrodes. Their operating principle is based on the difference in concentration of oxonium ions (H_3O^+) existing on either side of a very thin glass membrane (approx. 0.1 mm), which generates an electrical potential, known as the "membrane potential". This is proportional to the pH of the aqueous solution in which the electrode is immersed. This measurement technique, still used today for experimental laboratory studies, is associated with uncertainties that are too large (0.02 pH units) to allow estimation of inter-annual variations in ocean pH, which are of the order of a few thousandths of a pH unit.

A spectrophotometric method[6] using a specific dye, m-cresol purple, was first proposed in 1988 (Byrne *et al.*, 1988). The colour of the sample mixed with m-cresol changes from yellow to purple when the pH varies between 7.4 and 9.0. Measuring pH spectrophotometrically is much more precise than using glass electrodes, and can achieve uncertainties of the order of 0.003 pH units, making it possible to quantify the ongoing decrease in ocean pH levels.

From the 2000s onwards, autonomous sensors were developed to be installed on instrumented buoys in the ocean to measure pH at high frequency, without the need to visit the site and take samples to the laboratory for measurement. ISFET sensors (for "Ion-Sensitive Field Effect Transistor") use an ion-sensitive field effect transistor. When H^+ protons bind to the surface of the transistor, they alter its conductivity and generate a pH signal. Another technique combines a water sampler with pH spectrophotometric measurement. The idea is to take a water sample automatically at regular intervals using a small programmable pump, inject the dye into the sample and measure its absorbance to determine the pH[7].

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[6] A spectrophotometer is used to determine the concentration of a chemical species in a solution (in the case of pH, protons). To do this, the device measures the intensity of light passing through a sample at a given wavelength. More precisely, the spectrophotometer measures absorbance, i.e. the proportion of light radiation absorbed by the sample. The higher the absorbance, the higher the concentration.

[7] http://www.sunburstsensors.com/products/oceanographic-ph-sensor.html