OCEANOGRAPHY AND MARINE BIOLOGY SERIES

SEAS AND OCEANS SET

# Marine Ecosystems

## *Diversity and Functions*

**Edited by**
**André Monaco and Patrick Prouzet**

iSTE

WILEY

# Foreword

We have been asked by ISTE to stimulate work in the area of the environment. Therefore, we are proud to present the “Seas and Oceans” set of books, edited by André Monaco and Patrick Prouzet.

Both the content and the organization of this collection have largely been inspired by the reflection, initiatives and prospective works of a wide variety of national, European and international organizations in the field of the environment.

The “oceanographic” community, in France and internationally – which is recognized for the academic quality of the work it produces, and is determined that its research should be founded on a solid effort in the area of training and knowledge dissemination – was quick to respond to our call, and now offers this set of books, compiled under the skilled supervision of the two editing authors.

Within this community, there is a consensus about the need to promote an interdisciplinary “science of systems” – specifically in reference to the Earth’s own “system” – in an all-encompassing approach, with the aim of providing answers about the planet’s state, the way it works and the threats it faces, before going on to construct scenarios and lay down the elementary foundations needed for long-term, sustainable environment management, and for societies to adapt as required. This approach facilitates the shift of attention from this fundamental science of systems (based on the analysis of the processes at play, and the way in which they interact at all levels and between all the constituent parts making up the global system) to a “public” type of science, which is finalizable and participative, open to decisionmakers, managers and all those who are interested in the future of our planet.

In this community, terms such as “vulnerability”, “adaptation” and “sustainability” are commonly employed. We speak of various concepts, approaches or technologies, such as the value of ecosystems, heritage, “green” technologies, “blue” chemistry and renewable energies. Another foray into the field of civilian science lies in the adaptation of research to scales which are compatible with the societal, economic and legal issues, from global to regional to local.

All these aspects contribute to an in-depth understanding of the concept of an ecosystemic approach, the aim of which is the sustainable usage of natural resources, without affecting the quality, the structure or the function of the ecosystems involved. This concept is akin to the “socio-ecosystem approach” as defined by the Millennium Assessment (http://millenniumassessment.org).

In this context, where the complexity of natural systems is compounded with the complexity of societies, it has been difficult (if only because of how specialized the experts are in fairly reduced fields) to take into account the whole of the terrestrial system. Hence, in this editorial domain, the works in the “Seas and Oceans” set are limited to fluid envelopes and their interfaces. In that context, “sea” must be understood in the generic sense, as a general definition of bodies of salt water, as an environment. This includes epicontinental seas, semi-enclosed seas, enclosed seas, or coastal lakes, all of which are home to significant biodiversity and are highly susceptible to environmental impacts. “Ocean”, on the other hand, denotes the environmental system, which has a crucial impact on the physical and biological operation of the terrestrial system –

particularly in terms of climate regulation, but also in terms of the enormous reservoir of resources they constitute, covering 71% of the planet’s surface, with a volume of 1,370 million $km^3$ of water.

This set of books covers all of these areas, examined from various aspects by specialists in the field: biological, physical or chemical function, biodiversity, vulnerability to climatic impacts, various uses, etc. The systemic approach and the emphasis placed on the available resources will guide readers to aspects of value-creation, governance and public policy. The long-term observation techniques used, new techniques and modeling are also taken into account; they are indispensable tools for the understanding of the dynamics and the integral functioning of the systems.

Finally, treatises will be included which are devoted to methodological or technical aspects.

The project thus conceived has been well received by numerous scientists renowned for their expertise. They belong to a wide variety of French national and international organizations, focusing on the environment.

These experts deserve our heartfelt thanks for committing to this effort in terms of putting their knowledge across and making it accessible, thus providing current students with the fundaments of knowledge which will help open the door to the broad range of careers that the area of the environment holds. These books are also addressed to a wider audience, including local or national governors, players in the decision-making authorities, or indeed “ordinary” citizens looking to be informed by the most authoritative sources.

Our warmest thanks go to André Monaco and Patrick Prouzet for their devotion and perseverance in service of the success of this enterprise.

Finally, we must thank the CNRS and Ifremer for the interest they have shown in this collection and for their financial aid, and we are very grateful to the numerous universities and other organizations which, through their researchers and engineers, have made the results of their reflections and activities available to this instructional corpus.

André MARIOTTI
Professor Emeritus at University Pierre and Marie Curie
Honorary Member of the Institut Universitaire de France
France
Jean-Charles POMEROL
Professor Emeritus at University Pierre and Marie Curie
France

# 1

# Marine Biosphere, Carbonate Systems and the Carbon Cycle

## 1.1. Introduction

It is now accepted that the recent increase in the concentration of carbon dioxide ($CO_2$) in the atmosphere is a consequence of human activities, in particular the combustion of fossil fuels and the production of cement. Approximately 30% of $CO_2$ emissions are absorbed by the ocean, which clearly indicates the importance of the sea in the regulation of the level of atmospheric $CO_2$. Once absorbed by the ocean, this carbon becomes an important parameter in biogeochemical cycles.

For several million years, the concentration of $CO_2$ in the atmosphere has shown cyclic variations directly linked to global changes in volume. These changes occur at regular intervals of 100,000, 40,000 and 23,000 years (Figure 1.1) which represent the Earth's orbit about the Sun; these phases control the insolation on the surface of the Earth (solar forcing) and are responsible for the natural variability of the climate.

COMMENTS ON FIGURE 1.1.– These parameters, each with their own frequency, combine together and cause climatic variations, particularly glacial/interglacial variations. The two curves to the bottom of the figure show: the variations in isotopes of oxygen in the plankton shells (SPECMAP) [MAR 87] which are determined by water temperature and the global volume of ice over the past 400,000 years. Ice cores entrap bubbles containing past atmospheres. The concentration of $CO_2$ in these bubbles (EPICA) [LUE 08] is very similar to that in the ocean, by identifying glacial (gray areas) and interglacial areas.

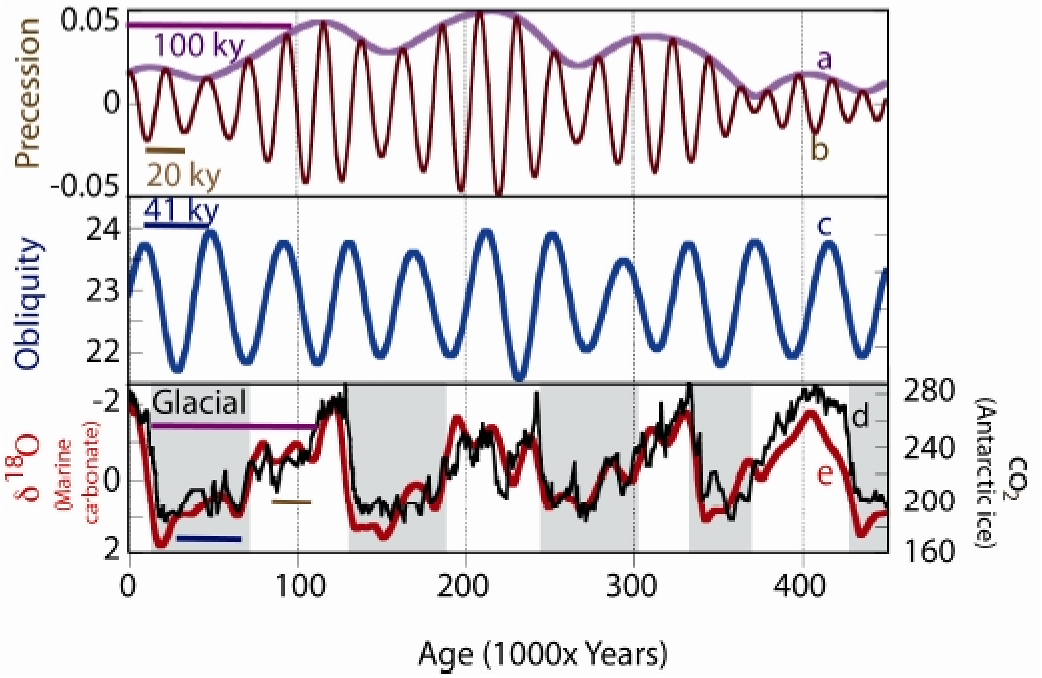

**Figure 1.1.** *Parameters of the Earth's orbit [LAS 04] molding the global climate ($CO_2$ concentration in ice core d), oxygen stable isotopes in marine sediments e), precession b) and obliquity c) influence the seasonal contrasts, eccentricity a) modulates (amplifies or not) precession effects (Beaufort, compilation of [LAS 04, LUE 08, MAR 87])*

The reasons why the atmospheric concentration of $CO_2$ follows climatic variations are still not fully understood, but the ocean could be responsible for their long term natural variations. In fact, the ocean surface layer contains an enormous reservoir of carbon than can react with the atmosphere over these orbital time scales. Marine organisms are of particular importance in these mechanisms as they help incorporate (pump) and transfer a large amount of carbon from the surface of the ocean to the deep sea and into sediments (sinks). Their role becomes crucial in the global carbon cycle.

If we know that human activities, by emitting large quantities of $CO_2$ into the atmosphere, disturb the biological fluxes of carbon in the ocean, it is extremely difficult to predict the response of marine ecosystems and what the future holds for natural carbon in the biological cycle. Studying marine sediments, which can be considered as historical archives of ocean ecology, allows us to better understand how the ocean participates in the carbon cycle and how marine biodiversity adapts to global changes. In the past, these changes in biodiversity have sometimes had very significant retroactive effects on the environment and climate.

This contribution does not intend to describe the chemistry of oceans or biogeochemical cycles, widely developed in the first volume of this set of books [BER 14, LEG 14]. As stated by Legendre [LEG 14], despite their low biomass, pelagic ecosystems are the driver of biogeochemical cycles in the oceans. In this context, we will focus in particular on calcareous phytoplankton in the dynamics of carbon and its role in the evolution of past and future climates. The complexity of these processes is why this system is often disregarded in experimental research, models and projections.

## 1.2. Marine organisms and carbon

Marine organisms are clearly adapted to the ocean properties, in which they live, but they also actively contribute to its composition; since organismal biology is based on the chemistry of carbon, this is particularly true for the concentration of carbon dissolved in the sea. In fact, marine organisms use carbon to build their tissues (organic form of carbon), many of which also form solid skeletons, particularly in the form of calcium carbonate (inorganic form of carbon). The concentrations of dissolved and particulate carbon therefore change according to the mass and activity of these organisms. Two equations can express the dual effect of this activity on dissolved carbon: on the one hand, carbon sequestration by photosynthesis into their tissues [1.1] and, on the other hand, the release of $CO_2$ upon the construction of their carbonaceous skeleton from bicarbonate and dissolved calcium [1.2]:

$$CO_2 + H_2O + \text{light} \rightarrow CH_2O \text{ (organic matter)} + O_2 \qquad [1.1]$$

$$Ca^{2+} + 2HCO_3^{-} \rightarrow CaCO_3 \text{ (carbonate)} + CO_2 + H_2O \qquad [1.2]$$

These processes can be reversed depending on the environmental conditions. In addition, if the organic matter produced is used by another organism (grazing, predation), this will release carbon dioxide; however, if it is buried in the sediments; the carbon will be trapped, sometimes for very long periods of time (sequestration). With regard to the carbonates that form the skeletons (calcification), they will be either buried in sediment or dissolved in the ocean.

Calcification and biomineralization will depend on the biodiversity of the organisms; different species will not produce the same quantity of matter, skeletons do not have the same degree of calcification as they are produced at different paces. We will therefore see how marine biodiversity impacts the global carbon cycle and therefore climate.

## 1.3. Variability in the production of organic matter

During photosynthesis, marine algae absorb dissolved $CO_2$ to produce their biomass, thereby releasing oxygen (equation [1.1]). The algal production is not distributed uniformly throughout the ocean. Most multicellular algae live on the seabed and on a substrate; they are therefore known as benthic; and their distribution is limited to the shallowest depths of the ocean where sunlight can penetrate. On the contrary, algae that constitute the phytoplankton are almost all unicellular and floating; they are widely distributed along oceanic margins, and beyond, over a maximum of approximately 200 m wide in the water column.

Continental margins are generally much more productive in terms of organic matter than zones situated in the center of oceanic basins. In fact, rivers feed the coastal zones with nutritive salts (nitrogen, phosphorus, etc.), required for the growth of phytoplankton. Offshore, in the pelagic zone, this lateral input is increasingly less as one strays from the continents. The wind sometimes brings dust rich in nutritive salts, but these fluxes rarely compensate for this deficit.

Pelagic phytoplankton that lives exclusively in the photic zone (zone exposed to light) depletes the nutrient stores during photosynthesis; the only way to regenerate this stock at the surface is by the vertical pumping of nutritive salts in the deep sea (>200 m). These vertical nutrient transfers, required for pelagic life, are only produced by updrafts caused by gusts of wind in favorable directions (upwelling) or by the deep mixing of surface layers during episodes of strong winds.

One example of this mechanism can be found in the Indian Ocean where monsoon winds are powerful enough to break down the vertical stratification and allow high phytoplanktonic production by fertilization at depth. This mixing acts over a certain depth and is called the mixed layer; when it reaches the thermocline that separates warm surface waters from cold deep waters, the nutritive salts then diffuse towards the surface. We can then easily understand that during periods favored by strong Indian monsoons, or strong trade winds, offshore of West Africa, oceanic primary production (produced by phytoplankton or PP) is reinforced.

Studying sediment cores taken from these zones has revealed that highly biologically productive periods alternate with depletions, and that these changes follow the rhythms of the Earth's orbit. Thus, primary production, expressed in grams of carbon per meter squared per year, has increased from 120 to 200 gC/m$^2$/yr, since the previous precession cycle of the equinoxes in the center of the Indian Ocean [BEA 97] or in the Banda Sea (Figure 1.2). By causing seasonal variations and by heating different tropical zones, these cycles cause the increase or decrease in winds above the Indian Ocean, beginning with oceanic production.

COMMENTS ON FIGURE 1.2.– Top: variations in organic productivity, common (calculated by EOF) to the entire tropical band in the Indian and Pacific Ocean [BEA 01] (continuous line and circles). The organic production varies according to the concentration of $CO_2$ measured in the core of Antarctic ice [LUE 08] (dotted line and full squares). Bottom: recording of the organic production (dotted line, full circles and vertical error bars) in the Banda Sea. It is highly dependent on the intensity of the Australian monsoon [BEA 10]. The monsoon activity deduced follows the rhythms of insolation which are parameters of the Earth's orbit (continuous line) [LAS 04]. This highlights the difference that can exist between the local and global variations.

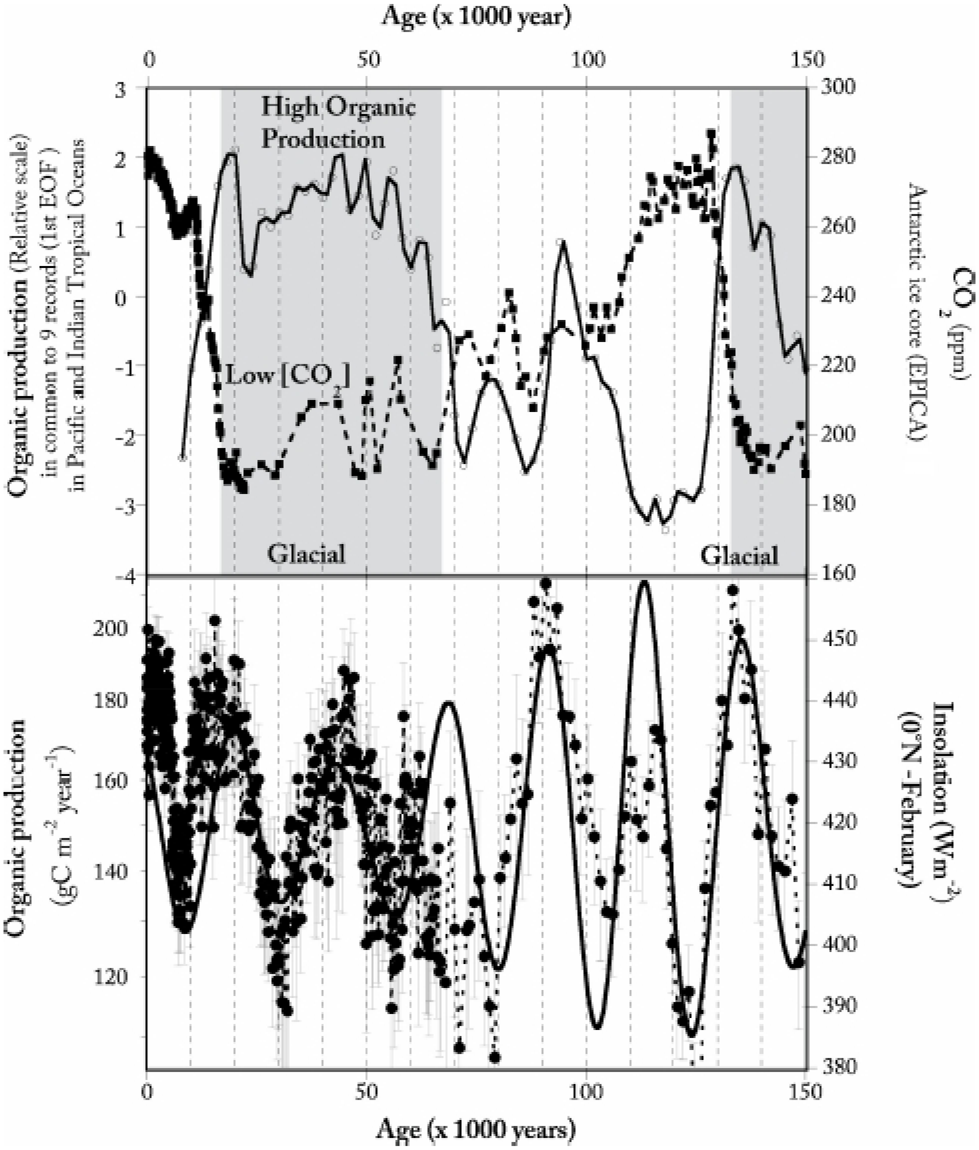

**Figure 1.2.** *Example of the evolution of organic production in the tropical zone over 150,000 years*

In this example, it is also clear that these changes in primary productivity are accompanied by significant variations in biodiversity. In the sediments deposited in the center of the Indian Ocean 20,000 years ago, 80% of fossil micro flora observed (Figure 1.3) is represented by species known to currently inhabit depths of 100 to 200 m beneath the ocean surface, at the lower limit of the photic zone, in conditions of very low levels of light. However, 10,000 years ago, this microflora represents only 10% of the assembly (assembly of a fossilized community); it has also been replaced by more diverse forms known to live between 0 and 100 m.

We can compare this location in the ocean 20,000 years ago to where we currently find the poorest zones of the central South Pacific (around Easter Island or North Pacific (Hawaii)). These zones, called gyres, represent oceanic deserts (except for areas close to islands) where planktonic organisms live at their deepest, to the extreme limits of light able to access nutritive salts. These zones are occupied by sparse ecological communities, especially at the surface and there are significant vertical differences in the composition of phytoplankton. In the central South Pacific, the specific composition at depth (example 150 m) is more similar to that of the north of the central North Atlantic, at the same depth, than those that live just below the surface. Longhurst [LON 98] defines the base of the mixing zone as the most significant ecological barrier that exists in the ocean. Biogeographical regions or biomes can be defined based on variations in some physicochemical parameters such as the depth of the thermocline and the photic zone, or seasonality.

## 1.4. From the biosphere to the atmosphere to climate

If climate changes greatly influence phytoplanktonic communities in the sea, in turn, these ecological changes can alter the $CO_2$ composition in the atmosphere and hence the climate. Similarly, global changes to the wind regime have significant consequences on the carbon cycle and marine biodiversity.

Currently, the global annual primary production is approximately 40–45 gigatons of carbon ($45 \times 10^9$ g). Most of this biomass is consumed by heterotrophic organisms (planktivores, carnivores and decomposers) and the mineralization of this organic matter will produce $CO_2$. Ultimately, only a small part falls to the oceanic depths where it is either consumed by heterotrophic benthic organisms, or buried in the sediments. In the former case only, carbon is removed from biogeochemical cycles, often for very long periods of time. We are therefore referring to exported primary production. Although this represents a very small fraction (0.02%) of what is produced at the ocean surface, this fraction of deposited carbon actually represents a significant carbon sink due to the immensity of the ocean surface; it is currently estimated to be more than 10 Mt ($10^7$ g) of carbon per year. Changes in climate will induce changes in the deposition rate of organic matter via changes to the general circulation speed or degree of oxygenation of the deep ocean which depends on the activity of the benthos; the absence of benthic organisms favors carbon sinks.

The issue that now deserves to be discussed is how a change to the oceanic biological production and its deposition rate as sediments alter the concentration of $CO_2$ in the atmosphere. This was the first hypothesis proposed by Broecker [BRO 82] to explain the discovery, in 1980, of lower levels of $CO_2$ in the atmosphere during glacial periods than during interglacial periods. This author proposes an increase in concentration of nutritive salts (essentially phosphate) which would favor organic production. In fact, the decrease in sea levels during the ice age would expose marine sediments rich in phosphate, deposited during the previous interglacial period, and transfer them into the ocean via rivers. This fertilization of the glacial ocean would have induced a greater sequestration of carbon.

Other reasons have been put forth to explain the decrease in concentration of atmospheric $CO_2$ during the ice age. Note, a better use of nutritive salts by phytoplankton in the Antarctic Ocean [FRA 97]; an increase in strong dustladen winds bringing iron into zones where this micronutrient is currently not found [MAR 90]; an increase in productivity resulting from a transfer of dissolved silica from the Antarctic Ocean towards the lower latitudes [MAT 02]; a decrease in the general depth of the thermocline at low latitudes which would have fertilized the ocean surface [BEA 01]; or even, an increase in biological production parallel with a decrease in carbonate production [BRO 82]. The latter point will be discussed later on.

Most of these hypotheses themselves cannot completely explain the decrease in concentration of atmospheric $CO_2$ during ice ages. Moreover, reconstructions of the primary production during these episodes do not always confirm the increases, and large local variations are observed.

At low latitudes, organic production seems to vary independently of global changes in climate [BEA 97] (Figure 1.2). At these latitudes, changes in organic productivity occur every 20,000 years which corresponds to local variations in seasonal insolation, whereas variations in global ice volume occur less frequently (every 41,000 and 100,000 years). Numerical simulations also indicate that local factors, for example wind strength and that of upwelling, are responsible for distribution structures and changes in production of organic matter. Sediments in the tropical zone of the Pacific and Indian Ocean also reveal that the organic production during the last ice age was 50% greater than that produced today (Figure 1.2).

However, many records of organic productivity reveal variations with a dynamic opposite to variations in concentrations of atmospheric $CO_2$ (Figure 1.2 top); but locally the variations may obey different rules (Figure 1.2 bottom).

At high latitudes (above 40°) and in many tropical regions (for example in the monsoon region), numerical simulations show an increase in PP during the ice age which implies greater sequestration of $CO_2$ during these periods. A compilation of many data from studies of sediments of the world’s oceans indicates that the exported organic production (including sediments) during the last maximum ice age is slightly higher than that of today. However, this variation does not appear to be enough to explain the differences in $CO_2$ between the glacial and interglacial period. As a result, even if the mechanism proposed by Broecker [BRO 82] cannot fully account for these variations, we know that the primary production has varied greatly in the past and contributed significantly to the atmospheric $CO_2$ dynamics. So, there is a feedback loop between climate and the marine biosphere, both influencing one another.

## 1.5. Carbonate production

Calcium carbonate forms the greatest reservoir of carbon on Earth [LEG 14] and many marine species produce shells based on this bio mineral. These secretions, just like organic production, play an important role in the chemistry of the oceans. Just as Broecker stated for organic production, Berger [BER 82] also mentioned changes in the production and conservation of biogenic carbonates to explain variations in the concentration of $CO_2$ in the atmosphere during glacial and interglacial periods.

The phenomena responsible for this relationship are more difficult to explain since they involve complex chemical processes. So, if we conventionally assume that the dissolution of limestone by acid produces carbon dioxide, in the ocean, this is the opposite reaction: the dissolution of limestone sequesters $CO_2$ and secretes $CO_2$. As expressed in equation [1.2], calcification (precipitation of $CaCO_3$) is accompanied by the release of $CO_2$ from the ocean into the atmosphere. This is what is called the carbonate counter-pump [WES 93].

## 1.5.1. *Importance of biological carbonate production in the evolution of the planet*

In the ocean, most calcification is of biological origin. Non-biological precipitations of carbonate are only produced in the presence of extreme concentrations of carbonate or bicarbonate ions. These conditions only currently exist in rare environments, at warm shallow depths with high evaporation, but they are responsible for the formation of carbonaceous rocks in the primitive ocean.

### 1.5.1.1. *The Neoproterozoic*

In the primitive ocean and before the first secretions of biological origin, chemical precipitations only operated in conditions where there was an over saturation of carbonate ions which therefore meant atmospheric $CO_2$ was not controlled by the ocean. Carbonate ions from the weathering of aluminosiliceous continental rocks are transported towards the ocean. It was shown that the carbon input into the ocean from erosion was greater than that released into the atmosphere by marine calcification; the content of $CO_2$ in the atmosphere would have progressively declined. For example, if the flow of carbon into the ocean is greater than 25% of the flow of carbon into the atmosphere, in only one million years, the atmosphere would be depleted of $CO_2$ [BER 97]; the

Earth’s surface would therefore have been covered in ice, without a greenhouse effect.

The biological carbonate production began 3.5 billion years ago, with stromatholiths from the activity of photosynthetic cyanobacteria. These would have dominated the production of carbonates for a long time but insufficiently so to decrease the saturation of oceans with carbonate ions from the erosion of continental rocks. An increase in continental erosion, sequestration of atmospheric $CO_2$ and a decrease in the greenhouse effect [DON 04] arose as a result of extreme glacial events. The oceans were certainly completely covered in ice; between 0.8 and 0.6 billion years ago, we find traces of glaciers up to the equator, which was called Snowball Earth by Kirschivink [KIR 92].

It therefore appears that carbonate ions deposited into the ocean were not used quickly enough by stromatoliths and the biological release of oceanic carbon into the atmosphere was too limited to prevent these extreme conditions from occurring.

#### 1.5.1.2. *The Paleozoic*

At the beginning of the Paleozoic (primary era), approximately 550,000,000 years ago, several different groups of organisms, mollusks, sponges, corals, arthropods, etc., began to produce carbonaceous skeletons in shallow environments. This revolution of marine biodiversity would have had consequences on atmospheric $CO_2$ concentrations.

The rate of carbonate production depended on the relative sea level height and the usable area for calcification, during periods of high sea levels (submerged continental shelves), the total carbonate production will be significant and will cause an increase in $CO_2$ in the atmosphere; this relates to relatively warm periods. During periods of low sea levels, there are fewer calcifying organisms in shallow zones, which will cause a decrease in the total marine carbonate production which will not be able to compensate for the carbonate input from the continents. In particular, this is the case of periods of tectonic activity and uplift of mountain ranges where erosion is great. If the glaciations were severe, they would not have had the same extensions and consequences as before this first revolution, as during Snowball Earth.

### 1.5.1.3. *Mesozoic revolution*

During the Triassic (220 million years ago), a group of unicellular algae, the coccolithophores, began to produce a carbonaceous skeleton made of microscopic plates (coccoliths) external to their cells. These microalgae can develop offshore due to their floating ability and rapidly colonize the oceans. From the Jurassic onwards, they are accompanied by planktonic for aminifera, which, despite also being unicellular, belong to the zooplankton. Most current coccolithophores have a diameter of between 2 and 15 µm whereas for aminifera usually have a diameter of up to several hundred micrometers (Figure 1.3). Despite their tiny size and their low weight (less than a nanogram), coccolithophores can produce very dense blooms extending over thousands of kilometers squared. The density of calcareous scales is so great that they can be detected by satellite images. Found at the bottom of oceans, remains of coccolithophores can contribute to the formation of huge quantities of light carbonate-rich sediments; the extreme example is chalk from the Cretaceous (from the Latin *Creta*) uniquely composed of coccolithophore remains (Figure 1.4).

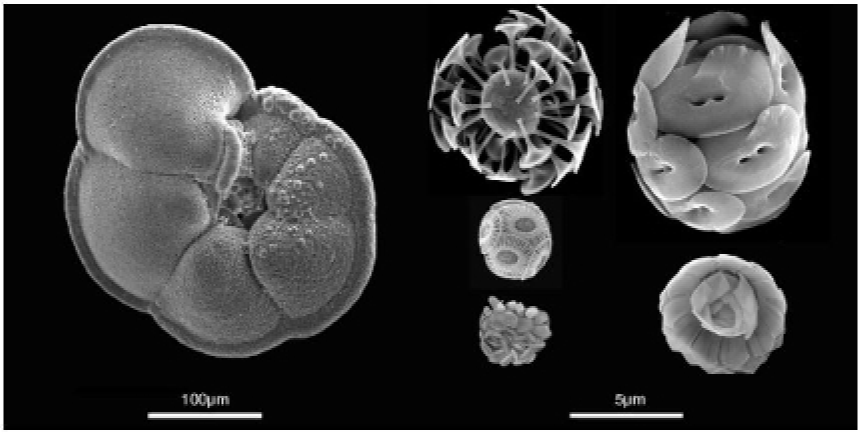

**Figure 1.3.** *Photographs taken using a scanning electron microscope of several representatives of the two main groups of pelagic calcifying organisms*

COMMENTS ON FIGURE 1.3.– To the left, planktonic for aminifera *Globorotalia menardii*; to the right, five coccolithophores (from left to right and top to bottom): *Discosphaera tubifera*, *Helicosphaera carteri*, *Emiliania huxleyi*, *Solisphaera galbula* and *Florisphaera profunda*. The two last species at the bottom left are typical of the deepest parts of the photic zone. Note the difference in scale (horizontal bars) for the foraminifera and for coccolithophores (author’s photos).

The colonization of the entire surface of the ocean by calcite-producing organisms was a major evolutionary event in the history of the climate. It was called the “mid-Mesozoic revolution” [RID 05] due to its high impact on marine chemistry. Pelagic calcification helped better stabilize the climate; even during glacial episodes of the quaternary period, it helped maintain an equilibrium between the production of marine carbonates and atmospheric carbon.

Numerical models have shown that carbonate concentrations have remained relatively stable over the past 100 million years, whereas they were two to three times greater and highly variable before the coccolithophores appeared (more than four times greater before the Paleozoic [RID 05]). This shows how important the role the diversity of the biosphere plays in the stability of the Earth's climate.

### 1.5.2. *Carbonate compensation depth*

Currently, coccolithophores and planktonic foraminifera produce the largest portion of calcium carbonate in the pelagic domain which represents 90% of the sea surface. However, if the open ocean contributes to more than half of the marine production, only a third approximately is accumulated in the form of $CaCO_3$. This difference is due to the fact that bio-mineral particles produced in shallow zones have a much greater chance of being buried than those produced offshore. So, aragonite crystals (one of two forms of $CaCO_3$) secreted by coralin tahiti certainly contribute to reef growth whereas calcite crystals (the other form of calcium carbonate), secreted at the surface by a coccolithophore tens of kilometers offshore of the reef, will not be buried in the ocean floor if they are too deep. In fact, beyond a depth of 4,000 m, calcite dissolves. It is estimated that 50–80% of carbonates that are secreted on continental margins are stored in coastal sediments, against 45% of carbonates produced in the open ocean. In comparison, each year, $11 \times 10^{12}$ moles of $CaCO_3$ accumulate in the pelagic zone and $7 \times 10^{12}$ moles of $CaCO_3$ in coral reefs [MIL 93]. Despite their better efficiency in storing calcium carbonate, coral reefs still accumulate less due to a relatively low useable area 0.6 million $km^2$ versus 106 million $km^2$ for the pelagic zone whose depth is less than 4,000 m. Carbonate particles dissolve below a certain depth mainly due to the high pressure; the solubilities of calcite and aragonite strongly depend on pressure, and at great depths, the pressure is great enough that $CaCO_3$ dissolves; this limited depth is called the lysocline.

First note, the transfer of particulate carbon towards the sea floor due to the aggregation of diverse particles produced on the surface and the ballast effect of coccoliths; since this falling of particles is referred to as “marine snow”, the deep sea is often represented as an alpine landscape with snowcapped peaks (white calcite and aragonite), and the deeper snow-free parts (without carbonates) (Figure 1.4). This physiographic limit corresponds to the base of the lysocline, carbonate compensation depth (CCD) below which there are no carbonate deposits. On the map of the central Pacific (Figure 1.4(c)) the white/black limit which corresponds to the mean depth of the lysocline (4 000 m +/– 900) represents the contrast between oceanic basalt (black) and the carbonates (light). A photo of the depths (Figure 1.3(b)), in this zone, at –2,000 m, shows that the sediments are whitish; a core sampled at this depth (Figure 1.4(c)) allows us to verify, from assessing samples using an electronic microscope, that the sediment is almost entirely composed of planktonic foraminifera (Figure 1.4(d)) and calcareous scales from coccolithophores (Figure 1.4(e)). In the same zone, but at greater depths, basalt occurs without being covered by sedimentary rock.

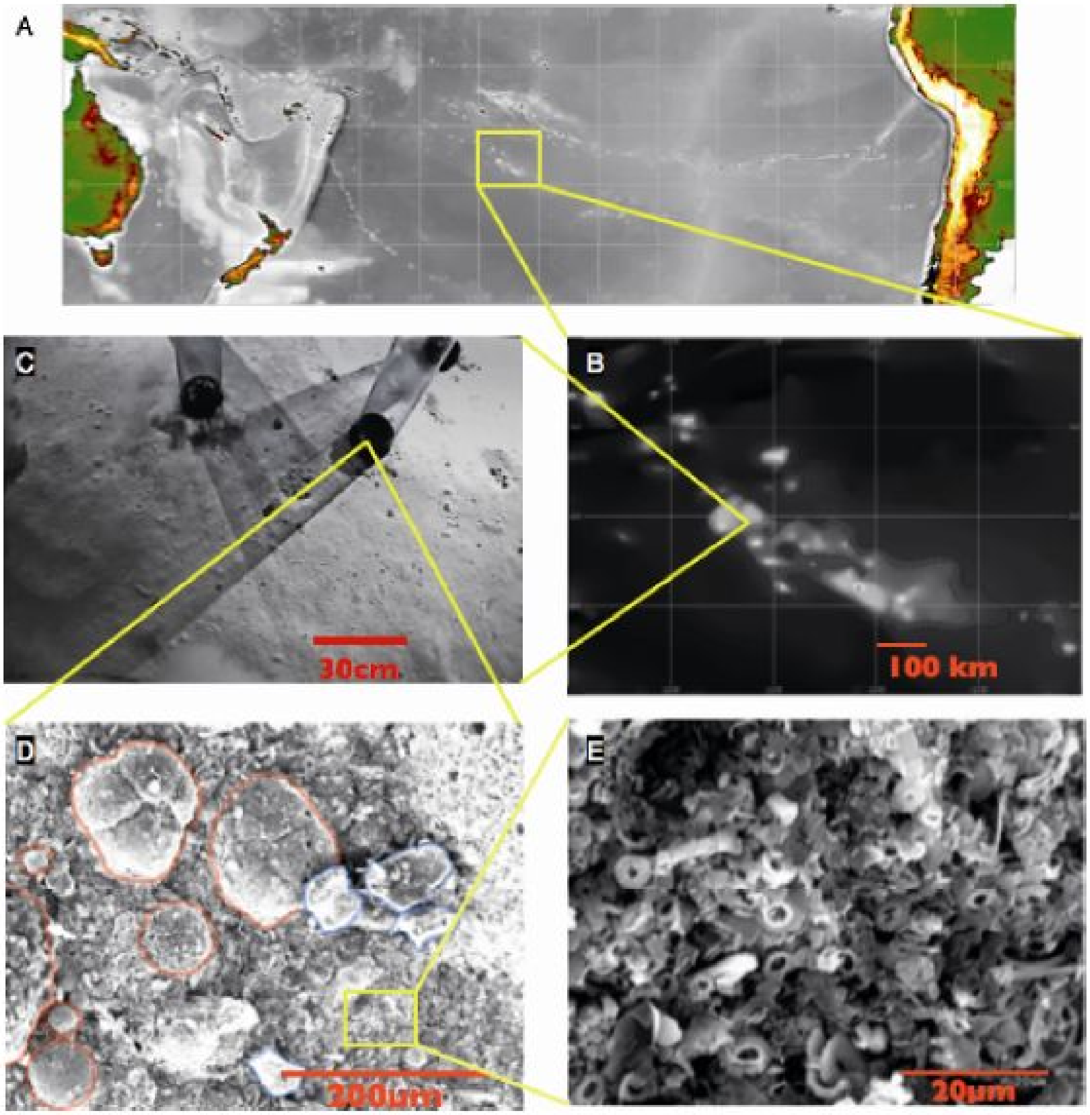

*Figure 1.4. Images of the deep sea in the Southern islands at a depth of 2,500 m (images from the oceanographic campaign SO2O4 Pacenpal by Beaufort, 2010)*

COMMENTS ON FIGURE 1.4.– (a) General map. (b) Detailed map; light areas are depths of less than 4,000 m occupied by carbonaceous sediments and the shaded areas are depths greater than 4,000 m where basalticrocks are found. (c) Photograph of the deep sea during the sampling of white calcareous sediment cores. (d) Photograph of the sediment viewed under a scanning electron microscope, showing the foraminifera (the largest particles) and their fragments (smaller identifiable elements). (e) Detailed image of (d) showing that the cement surrounding the foraminifera is exclusively composed of coccolithophore skeletons.

Carbonate compensation does not always occur at the same depth since the solubilities of calcite and aragonite also depend on the concentration of carbonate and calcium. So, a high productivity of $CaCO_3$ at the surface, during a coccolithophore bloom, will cause a high vertical flux of calcareous skeletons which, upon arrival at the CCD, will dissolve and release calcium and carbonate ions into the water; the increase in concentration of these ions will tend to displace the lysocline at depth. However, a zone of low carbonate production at the surface will have alysocline situated at middle depth. As long as there is a pelagic production of carbonate, the overall chemical concentration of Ca and carbonate ions in the ocean remains fairly constant and is redistributed by the currents.

The overall mechanism that transfers the sum of all chemical species of inorganic carbon or $\Sigma CO_2$ from the surface towards the sea floor and that maintains the high concentrations at depth is called the “carbonate-counter pump” and plays a key role in the regulation of the climate; Legendre [LEG 14] describes four types: physical, organic (or biological pump), carbonate-counter pump and the microbial pump.

### 1.5.3. *Carbonates and climate*

Very soon after the discovery of low concentrations of atmospheric $CO_2$ during ice ages, Berger [BER 82] stated that the possession of continental margins by coral reefs during deglaciation could explain a substantial part of the post-glacial increase in $CO_2$. During the last major ice age which occurred between 70,000 and 15,000 years ago, the volume of ice distributed over the continents was so large that it caused a decrease in the sea level by 120 m. Organic and carbonate production was limited to a small coastal fringe and the global production of $CaCO_3$ decreased to almost half [BER 82]. This decrease was slightly compensated for by the more constant production of pelagic carbonate following a deepening of the lysocline by approximately 1,000 m, as in the Pacific [FAR 89]. During deglaciation, the continental margins became gradually submerged and benthic calcification caused a rapid increase in reefs and therefore a gradual increase in $CO_2$ in the atmosphere.

The numerical modeling of this phenomenon shows that this amount of carbon accounts for a large part of the difference in concentration of atmospheric $CO_2$ between a glacial and an interglacial period. However, this scenario is often overlooked in current studies on the marine carbon cycle. The reason for the infrequent consideration of this phenomenon is due to the fact that it occurs as a result of climate change and therefore cannot initiate it. In fact, it requires that the sea levels rise as a result of warming. This initial warming cannot therefore be attributed to this phenomenon. Nevertheless, changes in the habitat area of marine organisms and ecological systems have certainly had a non-negligible retroactive effect on the climate variations during deglaciation.

Various experimental data show that during ice ages, the concentration of carbonate ions is greater, and hence the pelagic carbonate production is probably greater:

1) the planktonic foraminifera shells are then thicker and coccolithophores produce more calcified plates;

2) the pelagic production at low latitudes and particularly that of coccolithophorids is greater than that during interglacial periods;

3) as we have seen, the lysocline retreats.

So, a greater production of carbonate and a better conservation of carbonates will cause an increase in the concentration of atmospheric $CO_2$ which will mitigate the effects of glaciation. However, a precise quantification of the pelagic carbonate production and its conservation has rarely been carried out because of the complexity of its implementation.

## 1.6. The coupling of carbonaceous and organic productions

We have seen that the marine organic production as well as the carbonate production interfere, at different scales of time and space, with the concentration of $CO_2$. Some models play with this combination.

In this category, the most elegant is definitely that of the rain ratio by Archer and Maier-Reimer [ARC 94]. During the ice age, in the pelagic zone, there appears to have been an increase in organic productivity coupled with a decrease in carbonate productivity. So, carbon has a better chance of being sequestered in the sediments causing the observed decrease in carbon during this period. For these authors, a 40% decrease in the ratio of $CaCO_3$ in organic matter in sediment particles would be sufficient to explain the decrease in concentration of atmospheric $CO_2$ recorded during ice ages.

Several reasons could explain the decrease in this ratio; they are all linked to a major ecological change in the pelagic zone: the replacement of coccolithophores by diatoms, phytoplanktonic organisms by a siliceous skeleton. Diatoms would outcompete coccolithophores due to an influx of silicic acid whose sources, according to hypotheses, would be: wind (silicarich dust), rivers from exposed margins, or even an oceanic source of silica from the Antarctic.

This theory, still a very topical issue, has been faced with observations that contradict it:

> 1) as we saw above, the coccolithophores do not appear to have decreased in abundance nor in calcification; rather the opposite is observed;
>
> 2) in the cores from low and middle latitudes, we do not find a synchronous or large increase in the number of diatom skeletons.

We know that the process for storing marine organic matter is much more efficient than the aggregation of matter in suspension (marine snow). In this sense, calcareous coccolithophorid scales are the best vectors of carbon towards the sea floor and sedimentary sinks. In these conditions, if the coccolithophores were outcompeted by diatoms, the hypothesis of organic carbon sequestration in sediments would not be valid.

## 1.7. Modification of equilibria and consequences on marine life

Time constants play an important role in the carbon cycle; as described above, the marine carbon cycle follows the rhythms of global climate variations (Figure 1.1), but greater and more prolonged alterations, often of geodynamic origin (plate tectonics, uplift and erosion of mountain chains, large volcanic eruptions), greatly alter these rhythms. Note, in particular, the two best documented acidification events in the history of the Earth: one at the Permian-Triassic boundary, 250 million years ago, and the other at the Triassic-Jurassic boundary, 200 million years ago. These are also two of the most dramatic mass extinction events, with periods of volcanic activity where large amounts of $CO_2$ were released into the atmosphere, over a relatively long scale of time (several hundred thousand years) [WIG 01].

The effects of this were particularly felt by calcifying marine organisms, since most of them disappeared, as well as most species of coral, at the Triassic-Jurassic boundary. It took several millions years for new coral reef species to emerge from the few that survived [KIE 09]. Annual levels of $CO_2$ emissions during these events were much lower than today, but they lasted for a very long time; the chemical and ecological effects during these periods were certainly very different to what the ocean would encounter in the future [RID 05]. In fact, in the current conditions of high $CO_2$ emissions occurring over a relatively short period of time, it is difficult to predict the consequences on the marine biosphere and biogeochemical cycles.

Since the beginning of the Industrial Revolution, human activities have released huge quantities of $CO_2$ into the atmosphere, which is added to the natural carbon cycle. We have come to know the effects on the climate quite well and we are beginning to see the effects on the ocean via acidification. In fact, an increase in the $CO_2$ (partial pressure) in the atmosphere causes $CO_2$ to dissolve more readily in seawater, which consequently increases the $H^+$ ions and therefore decreases pH.

pH measurements over the past decades correspond exactly to numerical models, and emission projections allow us to predict ocean pH in the future. What we do not know is how to predict the consequences of this phenomenon on the marine biosphere. Many studies are currently being carried out on different groups of organisms with different methods (crop cultivation, *in situ* observation, etc.). One chapter in this set of books dedicated to the ocean covers the state of current research in this domain [GAT 14].

Logically, a decrease in pH would have consequences first and foremost on calcifying organisms and the disappearance of carbonate production would have severe consequences on the carbon cycle; in the future, the Earth could be heading towards a new ice age, worse than that two/three centuries ago with the little ice age.

Nevertheless, given the current trends, it is unlikely that this scenario will occur. Results from experiments on the possible effects of acidification on pelagic organisms, threatened in zones of high pH and different carbonate concentrations, are mixed [BEA 11]; they show a worrying general trend to decrease the degree of calcification of coccolithophore skeletons (Figure 1.5), but contrarily, in the most acidic waters of the world’s oceans, in the coastal resurgence of Chili and Peru, we find coccolithophores with more calcified skeletons than anywhere else. The photo in Figure 1.6 (left) shows a highly calcified *Emiliania huxleyi*, collected in water with a pH of 7.66 (global mean surface pH is 8.1) offshore of Peru in April 2014. Despite the low pH values in this resurgence high in $CO_2$, coccolithophores have managed to adapt possibly through physiological and energetic mechanisms.

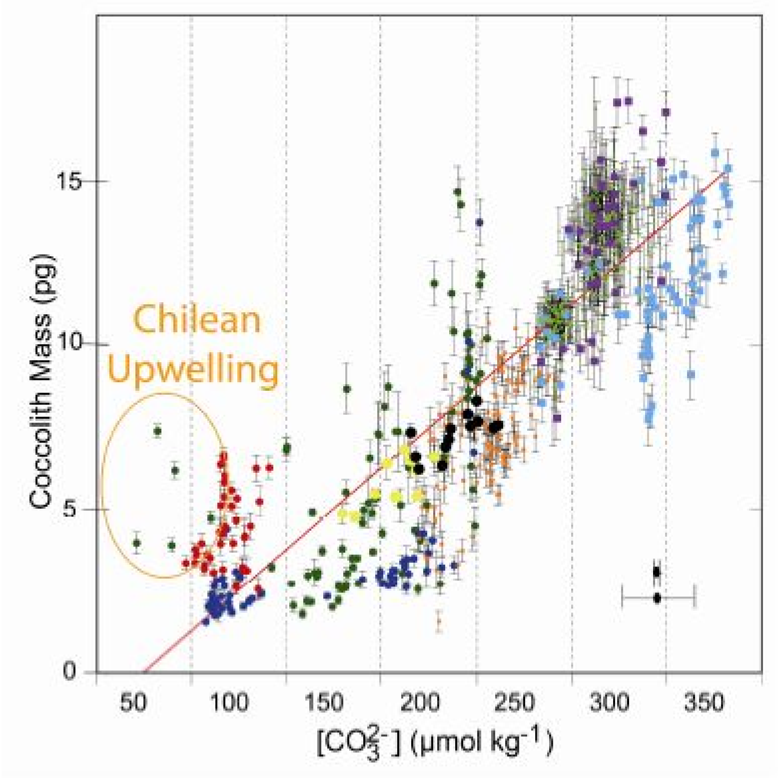

**Figure 1.5.** *Correlation between mass and calcified plates of coccolithophores (coccoliths) and the concentration of dissolved carbonate in seawater, in different regions of the current and past oceans (0 – 40,000 years ago) [BEA 11]*

COMMENTS ON FIGURE 1.5.– There is a positive relationship between mass (calcification of coccoliths) and carbonate concentration. In one of the most corrosive regions of the current ocean, upwelling from Chile (zone circled), we observe the opposite trend, with highly calcified coccoliths which should have disappeared due to the low carbonate concentration consistent with the trend indicated by regression line.

The models cannot predict that the ocean surface pH could drop to values lower than 7.6 over the next century, which makes the disappearance of these organisms possible and jeopardizes their role in the pelagic biosphere.